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EDITED BY

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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 an eighteenth 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 range from studies of some general problems in theoretical chemistry and diatomic interaction theory, to gap equations and instabilities for extended systems and conductivity properties of certain conjugated systems, to a discussion of the connection between the Hamiltonian and Liouvillian formalisms in the modern quantum theory of matter.

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

PER-OLOV LÖWDIN

The Theoretical Approach to Some Chemical Problems

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I. General Introduction

Quantum mechanics provides chemists with a definite formalism based on some general postulates. It allows them not only to calculate molecular properties but also to analyze the physical nature of chemical phenomena and, in this way, to realize a theoretical approach to chemical problems. To make this point clearer, we briefly recall the main features of the formalism of quantum chemistry.

In Schrödinger's formulation, the basic equation to be solved for describing a system of n electrons and N nuclei (i.e., an isolated molecule or supermolecule) may be formally written as:

$$\mathcal{H}\Gamma = W\Gamma \qquad (1)$$

Γ is a molecular wave function depending on the $3N + 3n$ nuclear and electronic coordinates. The Hamiltonian $\mathcal{H}$ is given by:

$$\mathcal{H} = T_{\mathrm{N}} + T_{\mathrm{e}} + V_{\mathrm{Ne}} + V_{\mathrm{ee}} + V_{\mathrm{NN}} \qquad (2)$$

where T_{N} and T_{e} are the kinetic operators of nuclei and electrons and V_{NN}, V_{ee}, and V_{Ne} are the potential operators of nuclear, electronic, and mixed

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origin, respectively. The eigenvalues of this Hamiltonian are the total energies (W) of the system under consideration.

Several approximations need to be introduced for solving Eq. (1). The first one is the well-known Born–Oppenheimer (1927) approximation which allows the separation of electronic and nuclear motions. This means that the total wave function may be separated into two parts such as:

$$\Gamma = F\psi \tag{3}$$

Electronic wave functions (ψ_i) are obtained by solving the corresponding electronic equation:

$$(T_{\mathrm{e}} + V_{\mathrm{Ne}} + V_{\mathrm{ee}} + V_{\mathrm{NN}})\psi = u\psi \tag{4}$$

for any nuclear configuration. Nuclear wave functions (F_j^i) are solutions of the equation:

$$(T_{\mathrm{N}} + u_i)F^i = W^i F^i \tag{5}$$

where the potential term u_i is the total electronic energy of a given state (i) of the (super)molecule. In the general case, u_i, which depends on $3N - 6$ (or $3N - 5$, for linear species) variables, is commonly called the potential energy hypersurface of the system. This function obeys the *generalized Hellmann–Feynman* (Hellmann, 1937; Feynman, 1939) *theorem:*

$$\frac{\partial u_i}{\partial \lambda} = \int \psi_i^* \frac{\partial H}{\partial \lambda} \psi_i \, d\tau \tag{6}$$

which may be used for analyzing the physical nature of the chemical bond.

Other approximations are needed for solving Eqs. (4) and (5). Most of the procedures for obtaining approximate solutions of the electronic equation are based on the independent-electron model which introduces the orbital and configuration concepts. In fact, it is well known that exact solutions of Eq. (4), taking account of electron spin, can be expanded in terms of Slater determinants which combine into appropriate configuration-state functions:

$$\Psi_i = \sum_{k=1}^{\infty} C_{ik} D_k \tag{7}$$

D_k is an antisymmetrized product of n spin orbitals which satisfies the indistinguishability and Pauli principles. The latter is actually a trivial consequence of a postulate of the greatest importance in quantum chemistry, i.e., the *antisymmetry principle* applying to total electronic wave functions. This postulate is very useful for justifying the Lewis (1916) theory of valence and for qualitatively describing the electronic structure of molecules (see Section II).

In practice, the D_k basis is truncated and approximate wave functions can be obtained using the configuration interaction (CI) method:

$$\Psi_i^{\mathrm{CI}} = \sum_{k=1}^{p} C_{ik}^{\mathrm{CI}} D_k \tag{8}$$

If only one configuration is retained, the approximate wave function of the ground state of a closed-shell system (containing $2n$ electrons) is a unique Slater determinant:

$$\Psi_{0_{\mathrm{approx}}} = |\Phi_1\bar{\Phi}_1 \cdot \cdot \cdot \Phi_n\bar{\Phi}_n| \tag{9}$$

The best orbitals are obtained in the framework of the restricted Hartree–Fock (RHF) method by solving the Hartree–Fock equations:

$$h^{\mathrm{HF}}\phi_i = \sum_j \varepsilon_{ji}\phi_j \tag{10}$$

or

$$h^{\mathrm{HF}}\boldsymbol{\phi} = \boldsymbol{\phi\varepsilon} \tag{11}$$

where $\boldsymbol{\varepsilon}$ is the matrix of the Lagrangian multipliers introduced to ensure the orthogonality during the extremization process.

It is well known that Eq. (11) has an infinity of solutions differing only by a unitary transformation. If we have n orbitals to determine, there are n^2 Lagrangian multipliers. The orthonormality condition introduces $n(n + 1)/2$ constraints, leaving $n(n - 1)/2$ arbitrary values. Putting these remaining parameters to zero, we suppress the off-diagonal elements and uniquely define Eqs. (10) in their canonical form:

$$h^{\mathrm{HF}}\phi_i = \varepsilon_{ii}\phi_i \tag{12}$$

This leads to the so-called canonical orbitals delocalized on the whole molecule. For determining their explicit form, the LCAO approximation is generally assumed and molecular orbitals are developed in terms of functions most often located on atoms, the atomic orbitals (χ). Thus:

$$\phi_i = \sum_{p=1}^{m} c_{pi}\chi_p \tag{13}$$

For any given set of functions χ_p, the best LCAO coefficients are obtained from Roothaan's (1951) equations, which may be written, in the usual notations:

$$\sum_p c_{pi}(h_{qp}^{\mathrm{HF}} - \varepsilon_i S_{qp}) = 0 \tag{14}$$

In fact, the truncation of the atomic basis set prevents reaching the so-called Hartree–Fock limit, and Roothaan's procedure leads to SCF molecular orbitals.

The above molecular orbital theory is always widely used either quantitatively by performing explicit calculations of molecular orbitals or qualitatively for rationalizing various kinds of experimental or theoretical data. As nicely shown by Gimarc (1979) in his comprehensive book "Molecular Structure and Bonding," qualitative MO theory allows an approach to many chemical problems related to molecular shapes and bond properties. Its most important achievement is the determination of reaction mechanisms by the well-known Woodward–Hoffmann (1970) rules and the general orientation rules proposed by Fukui (1970).

It is also interesting to use molecular orbitals localized in core, lone pairs, and bond regions, rather than fully delocalized canonical orbitals. A good choice of the remaining $n(n - 1)/2$ Lagrangian multipliers should lead to those localized orbitals, but such an *a priori* choice is hardly feasible. Most often, localized orbitals are determined by applying an adequate unitary transformation on previously obtained canonical orbitals:

$$\boldsymbol{\theta} = \boldsymbol{\phi}\mathbf{T} \tag{15}$$

where the matrix **T** is chosen on the basis of various criteria.

We have successively used the Magnasco–Perico (1967) external criterion and the Boys (1960) internal criterion. The results obtained by the Magnasco–Perico procedure allowed us (Leroy and Peeters, 1975) to study the transferable properties of localized orbitals and to elaborate a simple parametric method to construct wave functions for saturated hydrocarbons (Degand *et al.*, 1973), unsaturated hydrocarbons (Leroy and Peeters, 1974), heteroatomic aliphatic compounds (Clarisse *et al.*, 1976), and polymers (Peeters *et al.*, 1980). Furthermore, we have been able to analyze the concept of bond energy in terms of localized orbitals (Leroy *et al.*, 1975). A careful review on the utilization of transferability in MO theory has been realized by O'Leary *et al.* (1975).

The Boys internal criterion consists essentially in separating as much as possible the so-called centroids of charge of the various molecular orbitals. We have systematically used the Boys procedure for describing the electronic structure of chemical species and for determining the electronic mechanism of chemical reactions. The obtained results will be presented in Sections II and IV.

The SCF orbitals of open-shell systems may be obtained by the (spin) unrestricted Hartree–Fock (UHF) open-shell approach of Pople and Nesbet (1954). In this method, the orbitals associated with an α spin function are different from those associated with a β spin function. So, for a doublet ground state ($2n + 1$ electrons), the wave function is written as:

$$\Psi_{0_{\text{approx}}} = |\Phi_1\bar{\Phi}'_1 \cdots \Phi_n\bar{\Phi}'_n\Phi_{n+1}| \tag{16}$$

This is not an eigenfunction of the S^2 spin operator and therefore does not describe a pure spin state. An important advantage of the UHF method is to provide satisfactory spin densities of free radicals.

Moreover, the Boys procedure may also be used for localizing the singly occupied molecular orbitals obtained by the UHF approach (Peeters and Leroy, 1977). Thus, as shown in Sections II and IV, the electronic structure of open-shell systems and the mechanism of free-radical reactions can also be described in terms of the corresponding centroids of charge.

The electronic wave function of a definite state of a system allows us to calculate its molecular properties. These may be either observable values, measurable by some experiment and related to some operator, or purely theoretical quantities having or not a physical meaning. As stated by an important postulate of quantum mechanics, the expectation value of any observable is given by:

$$\langle G\rangle = \int \Psi^* G_{\text{op}} \Psi \, d\tau \tag{17}$$

the wave function being normalized.

In general, the operator G_{op} will be a sum of simpler ones depending on none, one, or two electrons at most:

$$G_{\text{op}} = G_0 + \sum_i G_1(i) + \frac{1}{2}\sum_i \sum_j G_2(i, j) \tag{18}$$

Thus, using the density matrix formalism, Eq. (17) may be written as (Daudel *et al.*, 1983, and references therein):

$$\langle G\rangle = G_0 + \int_{x'_1=x_1} G_1(1)\gamma(x_1x'_1)\, dx_1 + \frac{1}{2}\int_{\substack{x'_1=x_1\\ x'_2=x_2}} G_2(1, 2)\Gamma(x_1x_2x'_1x'_2)\, dx_1\, dx_2 \tag{19}$$

The above development does not introduce any approximation in the wave function. In the Hartree–Fock model, the first- and second-order density matrices are, respectively, given by:

$$\gamma^{\text{HF}}(x_1x'_1) = \sum_i \phi_i^*(x_1)\phi_i(x'_1) \tag{20}$$

and

$$\Gamma^{\mathrm{HF}}(x_1x_2x_1'x_2') = (1 - P_{12})\gamma^{\mathrm{HF}}(x_1x_1')\gamma^{\mathrm{HF}}(x_2x_2') \tag{21}$$

The latter expression clearly shows that Hartree–Fock wave functions are not properly correlated: they allow two electrons of opposite spin to simultaneously occupy a same elementary volume of an atomic or molecular space. Consequently, two-electron properties which are completely determined by the second-order density matrix cannot be correctly evaluated at the Hartree–Fock level and, *a fortiori*, from approximate SCF wave functions. On the contrary, satisfactory values of one-electron properties may be generally provided by those functions, at least in the case of closed-shell systems. However, due to the large contribution of pair correlation, the energy changes associated with the so-called isodesmic processes (Hehre *et al.*, 1970) can be reasonably well predicted at the Hartree–Fock level and also using SCF wave functions. Indeed, in that case, correlation errors approximately balance each other.

Furthermore, interesting properties may be deduced either directly from the potential energy hypersurface of the system under consideration or by solving the nuclear equation. So, for example, a careful analysis of the function u_0 of the ground state of a supermolecule allows us to determine not only equilibrium and transition structures but also reaction pathways at 0 K.

Neglecting the coupling between rotation and vibration, the nuclear equation of a polyatomic system can be separated into three equations describing the translational, rotational, and vibrational motions, respectively. Moreover, assuming the quadratic approximation, the polyatomic system may be considered as a superposition of diatomic harmonic oscillators. Thus, using a locally adapted quadratic surface around each stationary point, it is possible to perform the vibrational analysis of the corresponding equilibrium or transition structure. The rotational energy levels are also easy to determine in the framework of the rigid rotator approximation. So, the thermal and zero-point energy (ZPE) corrections may be calculated in order to deduce the thermodynamical properties of the system under consideration, by using the classical formalism of statistical thermodynamics. For example, the enthalpy of any species at temperature T is given by

$$H(T) = Nu_0(e) + 4RT + N\sum_j \frac{h\nu_j}{2} + N\sum_j \frac{h\nu_j}{e^{h\nu_j/kT} - 1} \tag{22}$$

where $u_0(e)$ is the electronic energy of the corresponding equilibrium structure and ν_j is the frequency of the jth normal mode of vibration. As to $\Delta G^0(T)$ of a given reaction, it may be written:

$$\Delta G^0(T) = \Delta U^0(0) - RT \ln \prod_i \left(\frac{Z_i^0}{N}\right)^{k_i N_i} \tag{23}$$

where Z_i^0 is the partition function of the ith constituent of the system. And finally, the equilibrium constant in terms of partial pressures is given by:

$$K_p(T) = \prod_i \left(\frac{Z_i^0}{N}\right)^{k_i N_i} e^{-\Delta U^0(0)/RT} \tag{24}$$

The reliability of the above theoretical results obviously depends on the quality of the hypersurface. At the SCF level, only the parts of the surface locally adapted around the stationary points corresponding to equilibrium structures are relatively accurate. For example, the SCF vibrational frequencies are overestimated with respect to experimental data by approximately 10% (Sana, 1981a). SCF heats of reaction and equilibrium constants are generally not satisfactory except for the transformations in which the number of electron pairs is conserved and, particularly, for isodesmic reactions.

Finally, potential energy hypersurfaces may be used for calculating the rate constant of elementary processes either in the framework of the transition-state theory (Glasstone *et al.*, 1941) or by performing classical trajectories calculations.

In the transition-state theory, the rate constant of a bimolecular process is written, in concentration units (Daudel *et al.*, 1983):

$$k_c = (kT/h)e^2 \exp(-\Delta U_c^\ddagger/RT) \exp(\Delta S_c^\ddagger/R) \tag{25}$$

where $\Delta U_c^\ddagger$ and $\Delta S_c^\ddagger$ are, respectively, the activation energy and the activation entropy and k is the Boltzmann constant. Three kinds of "activation energy" may actually be defined:

1. The true activation energy, i.e., the experimental Arrhenius activation energy which corresponds to $\Delta U_c^\ddagger$:

$$\Delta U_c^\ddagger = N\Delta u_0^\ddagger + \Delta(\mathrm{ZPE})^\ddagger + \Delta[U(T) - U(0)]^\ddagger \tag{26}$$

2. The activation barrier at 0 K:

$$\Delta \varepsilon^\ddagger = N\Delta u_0^\ddagger + \Delta(\mathrm{ZPE})^\ddagger \tag{27}$$

3. The activation barrier at 0 K without the ZPE correction term, $N\Delta u_0^\ddagger$, directly deduced from the electronic energies of the transition state and the reactants.

The preexponential factor of the Arrhenius equation is explicitly given by:

$$A_c = (kT/h)e^2 \exp(\Delta S_c^\ddagger/R) \tag{28}$$

or, in terms of standard entropies:

$$A_c = (kT^2/h)R'e^2 \exp(\Delta S^{\ddagger}/R) \tag{29}$$

R' being the ideal gas constant in liter-atmosphere. The expression of k_c [Eq. (25)] can be improved by taking account of the transmission coefficient and the tunneling correction (Christov, 1980). The accuracy of the results obtained by the above formalism depends once again on the quality of the potential energy hypersurface, which must be calculated beyond the Hartree–Fock approximation, and also on the validity of the transition-state model itself, including eventual correction terms. One particularly knows that there is no unique approach to the tunneling effect (Wigner, 1933; Goldanskii, 1959; Christov, 1972).

The wave-mechanical treatment of molecular collisions leading to chemical reactions remains a very difficult problem even in the framework of the Born–Oppenheimer approximation. It is the reason why a classical treatment is usually made (Karplus *et al.*, 1965). It consists in computing the trajectories of the nuclei by solving Hamilton's equations of classical mechanics, the potential introduced in these equations being the total electronic energy u_0 (of the ground state if thermal reactions are considered). Due to the great difficulty in obtaining accurate potential energy functions for actual systems, not many rate constant calculations have been realized up to now by this procedure.

The purpose of this article is to describe our limited contribution to the study of the chemical problems mentioned in this introduction. We shall successively envisage the electronic structure, the thermodynamical properties, and the reactivity of chemical species. Most of our theoretical results have been obtained at the SCF level using the localized orbital approach.

II. The Electronic Structure of Chemical Species

A. The Lewis Approach

The Lewis (1916) theory of valence may be considered as the first serious attempt to account for both polar and nonpolar bonds and, consequently, to describe the electronic structure of any chemical species. This theory is based on the famous *octet rule,* which may be stated as "every atom tends to acquire eight electrons in its outer shell, those being normally arranged in *pairs* at the four corners of a tetrahedron." Moreover, assuming the interpenetrability of atomic shells, Lewis shows that, in a nonpolar compound, each atom can satisfy the octet rule by *sharing* one or more *electron pairs* with the neighboring atom(s). This pairing of elec-

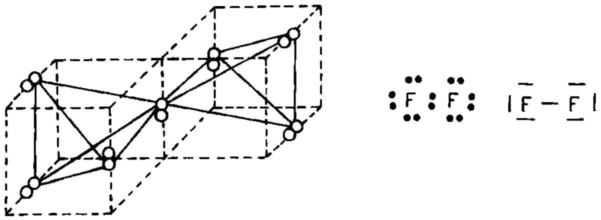


Fig. 1. Lewis and modern representations of the F_2 molecule.

trons leading to (stable) octets is identified as the "driving force" for covalent bond formation. In Lewis formulas each (bonding or nonbonding) electron pair is represented by a pair of dots (Fig. 1).

Obviously the Lewis theory of valence is unable to provide any satisfactory explanation of the stability and the physical origin of the chemical bond. Moreover, Lewis did not really understand the mechanism of the pairing of electrons. However, as shown below, quantum mechanics confirms very nicely most of the intuitive ideas of Lewis and consequently the essential features of its chemical formulas.

B. Quantum-Mechanical Approaches

1. *The Utilization of General Theorems and Postulates*

a. The antisymmetry principle. It is well known that taking account of the spin, the indistinguishability of electrons, and the antisymmetry principle, the total wave function of a two-electron system must obey the relation:

$$\Psi(M_1\omega_1; M_2\omega_2) = -\Psi(M_2\omega_2; M_1\omega_1) \qquad (30)$$

Thus, choosing $M_1 = M_2 = M$ and $\omega_1 = \omega_2 = \omega$, we may write:

$$\Psi(M\omega; M\omega) = -\Psi(M\omega; M\omega) = 0 \qquad (31)$$

which means that the probability of finding two electrons with the same spin in an elementary volume dv is strictly equal to zero. This conclusion is not valid for electrons of opposite spins. Then it follows that electrons of the same spin tend to avoid one another and to keep apart more than electrons of opposite spins. This is the rigorous justification of the pairing of electrons, but it must be realized that the electrons of a Lewis pair have opposite spins.

b. The generalized Hellmann–Feynman theorem. To analyze the physical nature of the chemical bond, two important theorems derived from the *generalized Hellmann–Feynman theorem* (Hellmann, 1937; Feynman, 1939) may be used. Let us first briefly recall the latter.

We consider a molecule containing a certain number of electrons moving in the field of fixed nuclei (Born–Oppenheimer approximation). Let H be the electronic Hamiltonian depending on a set of parameters λ_k ($1 \leq k \leq 3N - 5$ or $3N - 6$) specifying nuclear positions. If ψ and u represent the exact normalized wave function and energy for a nondegenerate electronic state, the generalized Hellmann–Feynman theorem states that:

$$\frac{\partial u}{\partial \lambda_k} = \int \psi^* \frac{\partial H}{\partial \lambda_k} \psi \, d\tau \tag{32}$$

As shown by various authors (Hurley, 1964, and references therein), for a given choice of parameters, the consequences of this theorem depend upon the coordinate system used for describing ψ and H. For illustrating this remark we consider the simplest molecule, H_2^+.

First, we use the coordinate system described in Fig. 2 and we choose as parameter λ_k a component of the position vector of one of the nuclei (x_a, y_a, or z_a; x_b, y_b, or z_b). Thus, Eq. (32) becomes:

$$\frac{\partial u}{\partial \lambda_k} = \int \psi^* \frac{\partial H}{\partial \lambda_k} \psi \, dv = -F_{\lambda_k} \tag{33}$$

where $\lambda = x, y, z$, $k = a, b$, and F_{λ_k} is the λ-component of the force acting on nucleus k. The electronic Hamiltonian may be written (in a.u.):

$$H = T + V = -\tfrac{1}{2}\nabla^2_{xyz} - 1/r_a - 1/r_b + 1/R \tag{34}$$

where

$$r_a = [x^2 + (y - y_a)^2 + z^2]^{1/2} \tag{35}$$

$$r_b = [x^2 + (y - y_b)^2 + z^2]^{1/2} \tag{36}$$

$$R = y_b - y_a \tag{37}$$

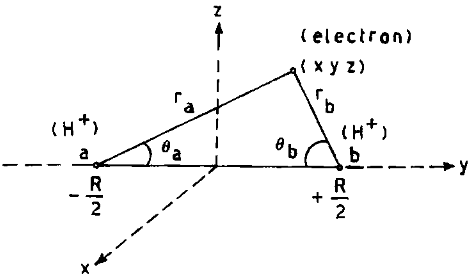


Fig. 2. Cartesian coordinate system for H_2^+.

It is easy to show that the force acting on nucleus a is given by:

$$\vec{F}_a = \vec{e}_2 \int \rho(xyz) \frac{\cos \theta_a}{r_a^2} dv - \vec{e}_2 \frac{1}{R^2} \tag{38}$$

where $\vec{e}_2$ is the unit vector lying on the y axis and $\rho(xyz)$ is the electronic density. A similar expression is obtained for the force acting on nucleus b:

$$\vec{F}_b = \vec{e}_2 \frac{1}{R^2} - \vec{e}_2 \int \rho(xyz) \frac{\cos \theta_b}{r_b^2} dv = -\vec{F}_a \tag{39}$$

The above formalism may be generalized to any homonuclear diatomic molecule (and to all other molecular species, but those will not be explicitly considered here). Then, the force on nucleus a is given by:

$$\vec{F}_a = \vec{e}_2 Z_a \left[\int \rho(xyz) \frac{\cos \theta_a}{r_a^2} - \frac{Z_b}{R^2}\right] \tag{40}$$

where $Z_a = Z_b$.

Equation (40) is usually called the *electrostatic theorem*. This states that the force acting on any nucleus can be calculated by classical electrostatics from the quantum-mechanical charge distribution ρ of the electrons and the point charges Z_k of the other nuclei.

The formation of a stable molecule from two atoms, or, in other words, of a chemical bond between these atoms, requires that, for some distance between them (the so-called equilibrium distance, R_e), the mean force which attracts the nuclei one toward the other will be exactly equal to that which repels them. This necessary condition may be expressed as:

$$\frac{1}{2} \int \rho(xyz) \left[\frac{Z_a \cos \theta_a}{r_a^2} + \frac{Z_b \cos \theta_b}{r_b^2}\right] dv = \frac{Z_a Z_b}{R^2} \tag{41}$$

The term between square brackets depends on the electronic coordinates (x, y, z). Let us represent it by $f(xyz)$. As first pointed out by Berlin (1951), the quantity ρ is always positive but the function f may be positive or negative and also equal to zero (Fig. 3). Thus, the integral in Eq. (41) can be separated into regions where $f > 0$ and $f < 0$. This leads to the expression of the force which binds the nuclei:

$$\frac{1}{2} \int_{f>0} \rho(xyz) f(xyz)\, dv = -\frac{1}{2} \int_{f<0} \rho(xyz) f(xyz)\, dv + \frac{Z_a Z_b}{R^2} \tag{42}$$

electronic binding force = electronic and nuclear antibinding forces

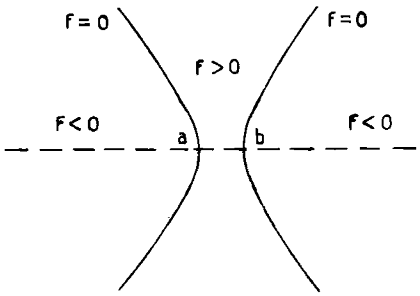


Fig. 3. Berlin diagram for homonuclear diatomic molecules.

Equation (42) shows that the binding force can only be large if the electronic density has important values in the internuclear region, which means that a certain number of electrons must visit this region. As stated by Feynman (1939): "It is clearly seen that concentrations of charge between atoms lead to strong attractive forces, and hence, are properly called valence bonds." This conclusion may be considered as a quantitative justification of the Lewis *electron pair sharing* concept.

In principle, only the wave function obtained by solving the Schrödinger equation allows us to calculate the electronic density in the various regions of a molecular space. However, as shown further, some qualitative information on this function can be provided by the Linnett (1966) approach.

If now ψ and H are expressed in terms of elliptical coordinates with foci at the nuclei a and b, it may be shown that:

$$du/dR = -(2\bar{T} + \bar{V})/R \tag{43}$$

with

$$\bar{T} = \int \psi^* T \psi \, d\tau, \qquad \bar{V} = \int \psi^* V \psi \, d\tau \tag{44}$$

Equation (43) is called the *virial theorem* (for a diatomic molecule). But, as

$$u = \bar{T} + \bar{V} \tag{45}$$

one easily obtains expressions for the mean kinetic and mean potential energies in terms of u and its derivative:

$$\bar{T} = -u - R\frac{du}{dR} \tag{46}$$

$$\bar{V} = 2u + R\frac{du}{dR} \tag{47}$$

As du/dR vanishes for $R = R_e$ and $R = \infty$, one finds:

$$\bar{T}(R_e) - \bar{T}(\infty) = D_e \tag{48}$$

$$\bar{V}(R_e) - \bar{V}(\infty) = -2D_e \tag{49}$$

the electronic dissociation energy D_e (which is a positive quantity) being given by:

$$u(R_e) - u(\infty) = -D_e \tag{50}$$

Moreover, the mean potential energy $\bar{V}$ is the sum of an electronic contribution $\bar{V}_e$ and a nuclear contribution $\bar{V}_N$ which vanishes for $R = \infty$. Thus, Eq. (49) can also be written:

$$\bar{V}_e(R_e) - \bar{V}_e(\infty) = -2D_e - \bar{V}_N(R_e) \tag{51}$$

Equations (48) and (50) show that the formation of a stable diatomic molecule from the free atoms is characterized by an increase of the mean electronic kinetic energy and a relatively more important decrease of the mean electronic potential energy. According to the above discussion, the chemical bond would result from the diminution of the mean potential energy of the electrons; at the equilibrium distance, this effect would prevail over the augmentation of $\bar{T}$ and $\bar{V}_n$:

$$\underset{<0}{\Delta\bar{V}_e(R_e)} + \underset{>0}{\Delta\bar{T}(R_e)} + \underset{>0}{\Delta\bar{V}_n(R_e)} = \underset{<0}{-D_e} \tag{52}$$

So it is seen that the joint utilization of the *antisymmetry principle* and of the formulas derived from the *generalized Hellmann–Feynman theorem* allows us to find a quantum-mechanical justification of the Lewis ideas (*electron pairing and sharing*) and to analyze the physical nature of the chemical bond.

To summarize, we may assume now that the formation of a covalent bond results from the concentration of (paired) electrons in the internuclear region, which leads to a strong binding force and a concomitant decrease of the mean electronic potential energy.

c. The Linnett theory. The Linnett (1966) approach to the electronic structure of chemical species is based on the concept of *charge and spin correlation* of electrons. This author uses the word "correlation" to mean the mutual effect that electrons have on one another's spatial positions due to Coulomb repulsions and the antisymmetry principle. Let us briefly summarize the main features of this approach.

Linnett examined first the behavior of a collection of uncharged particles which possess spin and which are confined to a circle. He showed that the particles split up into two sets according to their spin. In each set, their most probable disposition is that in which they keep as far apart as possible. If the two sets contain the same number of particles, the most probable configuration corresponds to paired particles. But if the two sets contain unequal numbers of particles, the probability does not depend on the mutual disposition of the two sets. If now charged particles having spin (such as electrons) are considered, the charge correlation must be taken into account. The correlation between electrons of the same spin is expected to be strong because of the cooperative effects of charge and spin correlation. On the other hand, the correlation between electrons of opposite spins will be relatively smaller because of the opposing effects of charge and spin correlation. Thus, in systems containing the same number of electrons of each spin, the charge correlation tends to reduce the probability of pair formation.

The above results have been generalized in three dimensions for describing the electronic structure of atoms. In that case, the most probable distribution of electrons on a sphere is to be examined. For atoms of the second row of the periodic table, the maximum number of electrons of each spin in the valence shell will be four. Assuming that electrons are approximately equidistant from the nucleus, the most probable electronic configuration of the outer shell of any second-row atom is easy to anticipate. The result obtained for neon is shown in Fig. 4 and is compared to the corresponding Lewis model completed by taking account of electron spin.

Thus, Linnett's theory replaces the Lewis octet, corresponding to four pairs of electrons of opposite spins, by the double quartet, corresponding to two sets of four electrons having the same spin within a given set.

The electronic structure of molecules can be anticipated using the *double-quartet rule,* which states that each atomic core tends to be surrounded by two tetrahedral sets (of electrons) weakly correlated. How-

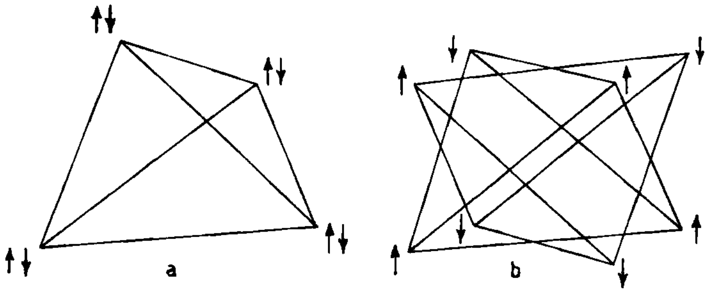
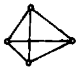
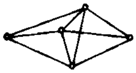
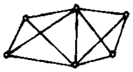
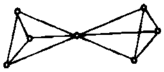


Fig. 4. Lewis (a) and Linnett's (b) electronic structure of neon outer shell.

TABLE I

MOST PROBABLE SPATIAL CONFIGURATIONS OF VARIOUS SETS OF ELECTRONS OF A GIVEN SPIN

Number	Spatial configuration
4	
5	
6	
7	

ever, in some cases, the two sets may be drawn together if this leads to a lowering of the potential energy of the system.

The Linnett procedure for finding the electronic structure of a molecule consists in localizing the valence electrons around the atomic cores by using the data of Table I, each core being generally placed inside a given tetrahedral set.

As an example, we give in Fig. 5 the Linnett structure of the oxygen molecule in its triplet ground state. It is seen that Linnett's formula is quite different from that of Lewis (also given in Fig. 5). This is obviously

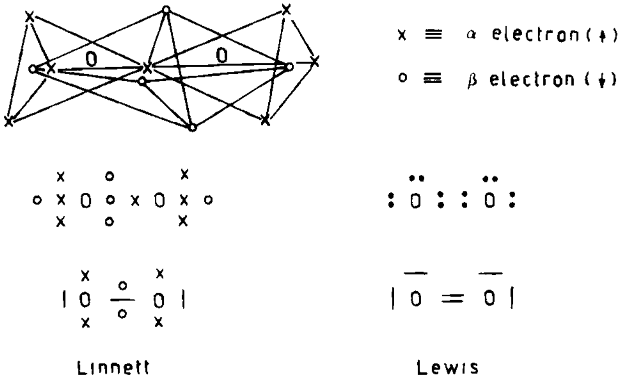
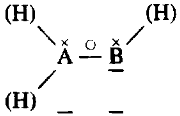


Fig. 5. Lewis and Linnett's formulas of the oxygen molecule.

TABLE II

LINNETT'S FORMULAS OF DIATOMIC SPECIES

Number of valence electrons	Compounds	Simplified Linnett's formulas
9	CN, N_2^+, CO	$\cdot\, A \equiv B\,|$
10	N_2, CN^-, CO, NO^+, C_2^{2-}	$|A \equiv B|$
11	NO, O_2^+	$|\overset{\times}{A} \overset{\circ}{=} \overset{\times}{B}|$
12	O_2, NO^-	$|\overset{\times}{\underset{\times}{A}} \overset{\circ}{\underset{\circ}{-}} \overset{\times}{\underset{\times}{B}}|$
13	O_2, HO_2, H_2NO, H_2NNH	
14	F_2, O_2^{2-}	$|\underline{\overline{A}} - \underline{\overline{B}}|$

due to the fact that Lewis was completely unaware of the existence of electron spin. Thus, in general, Linnett's theory is much more convenient for describing the electronic structure of open-shell species.

Other characteristic examples of Linnett's formulas are given in Table II. One will note that, except in the compounds containing nine valence electrons, each atomic core is surrounded by an octet made up of four α and four β electrons. It is also seen that in the most simplified representation of Linnett's structures, pairs of electrons of opposite spins are described by a line as in the modern Lewis formulas.

The results provided by Linnett's approach are more detailed than those of Lewis theory. Moreover, particularly in the case of unpaired electron species, they are in better agreement with spectroscopic and structural experimental data.

On the whole, Linnett's theory is very useful for rationalizing the structure, the stability, and even the reactivity of compounds containing up to four atoms. However, it may not be easily extended to larger molecules. Indeed, for those systems, its use becomes generally very intuitive and its results as ambiguous as those of resonance theory.

2. *Computational Approaches*

a. Introduction. Although the following discussions will be devoted to the *partitioning* and *functional facets* of the chemical bond (Daudel, 1976), we shall briefly recall, in this introduction, some other qualitative or computational approaches to the electronic structure of chemical species.

The shell model for diatomic molecules (Herzberg, 1939) is built up from the energetic diagram of symmetry orbitals. Among other interesting results, this qualitative model leads to the electronic structure of those compounds by using the concept of *bond order* (half the number of bonding electrons). The chemical formulas obtained in this way generally agree with the corresponding Lewis and (or) Linnett structures. However, some discrepancies are noticeable. So, in Herzberg's model, $\dot{N}O$ and $\dot{C}N$ would have similar electronic structures, which is not supported by Linnett's formulas nor by experimental properties of these radicals, such as their electron affinity and self-reactivity. It is indeed well known that $\dot{N}O$ is a stable species, and $\dot{C}N$, a transient radical.

A very detailed electrostatic interpretation of chemical binding has been given by Bader *et al.* (1967) by calculating the one-electron density distributions and the forces which they exert on the nuclei in the second-row homonuclear diatomic molecules. In this way, these authors could give a precise definition of the terms binding, nonbinding, and antibinding using a Berlin's *f*-function per orbital. More recently, Koga *et al.* (1980, 1982; Koga and Morita, 1980) generalized this approach more quantitatively in the case of H_2^+ and HeH^{2+} systems.

The role of the kinetic energy operator, especially its bond-parallel component, has been carefully analyzed by Ruedenberg (1962) in his comprehensive paper on the physical nature of the chemical bond. This author reaches the conclusion that "the effect of electron sharing upon the kinetic energy is the crucial effect" for the formation of a chemical bond. More explicitly, "the specific cause" for covalent binding is that "the kinetic energy of the shared electron increases less rapidly than that of the unshared electron." On the other hand, in a recent paper on the analysis of the covalent bond, Hurley (1982) definitely clarifies "the paradoxical role of the kinetic energy operator in the formation of the covalent bond." Using the virial and electrostatic theorems, he demonstrates that "If, and only if, the kinetic energy drops as the fragments are brought together, a stable molecule will be formed. Furthermore, the magnitude of the drop in the electronic kinetic energy is a direct measure of the strength of the association or bond."

Qualitative information on chemical binding can be directly obtained from the electronic wave function which allows us to calculate the electron density $\rho(M)$ and the difference density function $\delta(M)$ (Daudel, 1952).

The electron density is nothing more than the reduced first-order density matrix $\gamma(r_1 r_1')$, where $r_1 = r_1'$. Thus:

$$\rho(M) = \gamma(MM') \qquad \text{with} \quad M = M' \tag{53}$$

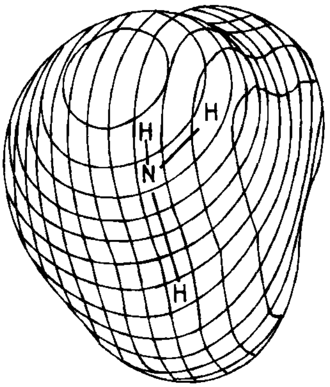


Fig. 6. Isodensity surface [$\rho = 10^{-3}e(\text{a.u.})^{-3}$] of the ammonia molecule.

This function is commonly represented by maps showing isodensity lines in some selected planes. Such maps do not generally provide clear information on the chemical bonds in the compound under consideration. However, a representation of $\rho(M)$ by dots whose degree of darkness is related to the value of electron density at the corresponding point may be used to qualitatively estimate the strength of the chemical bonds (Daudel *et al.*, 1983).

On the other hand, the shape of a molecule can be described by a selected isodensity surface as shown in Fig. 6 for the NH_3 molecule. In general, the volume inside the surface defined by $\rho = 10^{-3}e(\text{a.u.})^{-3}$ approximately "contains" all the particles of the corresponding species. Thus, it may be considered as a "molecular volume." Its partitioning in pseudologes will be described further. Some typical results obtained at the SCF level using the STO-3G basis set (Hehre *et al.*, 1969) are collected in Table III. Molecular volumes are compared with the corresponding available van der Waals volumes. Theoretical results are systematically larger but the correlation between the two series of values is satisfactory:

$$V_{\text{vdW}} = 1.7482 + 0.7206 V_{\text{th}} \quad \text{cm}^3/\text{g mole} \qquad (r = 0.9845) \qquad (54)$$

Otherwise, as shown by Bader *et al.* (1967), the density difference distribution may be taken as the pictorial representation of the "bond density" which is related to the forces exerted on the nuclei in the molecule.

The electronic structure of open-shell systems is better described by their spin density. This function is defined as the difference between the reduced first-order density matrices of α and β electrons, respectively, where $r_1 = r_1'$. Thus:

$$\rho_s(M) = \gamma^{\alpha}(MM') - \gamma^{\beta}(MM') \qquad \text{with} \quad M = M' \qquad (55)$$

TABLE III

THEORETICAL AND VAN DER WAALS MOLECULAR VOLUMES[a]: CALCULATED MEAN NUMBER OF ELECTRONS

Molecules	V_{th}[b]	n_{th}[b]	V_{vdW}[c]
LiH	19.51	3.84	—
BeH_2	24.63	5.87	—
BH	18.08	5.92	—
CH_4	22.88	9.91	17.12
NH_3	17.67	9.93	—
H_2O	13.17	9.95	—
HF	9.24	9.96	—
C_2H_2	25.41	13.91	20.84
C_2H_4	30.63	15.89	23.88
C_2H_6	35.83	17.87	27.34
CH_3NH_2	31.32	17.88	24.21
CH_3OH	27.40	17.89	21.71
CH_3F	23.95	17.91	19.39
BH_3NH_3	37.02	17.85	—

[a] All values in cm^3/g mole.

[b] Obtained by numerical integration (Tihange, 1978).

[c] Reid and Sherwood (1966).

The spin density, which can be either positive, negative, or equal to zero, integrates to the number of unpaired electrons. It provides a very simple expression of the expectation value of the S_z operator:

$$\langle S_z \rangle = \frac{1}{2} \int \rho_s(M)\, dv \tag{56}$$

Furthermore, its value at a given nucleus (N), $\rho_s(N)$, is connected with the corresponding isotropic hyperfine splitting constant measured by ESR spectroscopy. However, it is well known that Gaussian basis sets are inadequate near the nuclei because they do not satisfy the cusp condition. Consequently, they fail to predict spin densities at the nuclei and the corresponding isotropic hyperfine splitting constants. Still the sign of the spin density is generally well predicted. So, this function gives interesting information on spin polarization and delocalization effects and, in this way, on the type of any free radical (atom-centered or delocalized species). It is noticeable that theoretical (4-31G) results confirm the qualitative spin polarization and hyperconjugation models (Leroy, 1981). In-

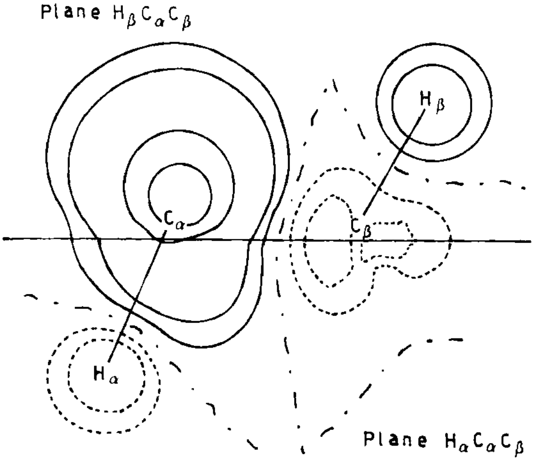


Fig. 7. Spin density of the ethyl radical in $H_\beta C_\alpha C_\beta$ and $H_\alpha C_\alpha C_\beta$ planes. Contours: (——) positive, (· · ·) negative, and (-----) zero values, respectively.

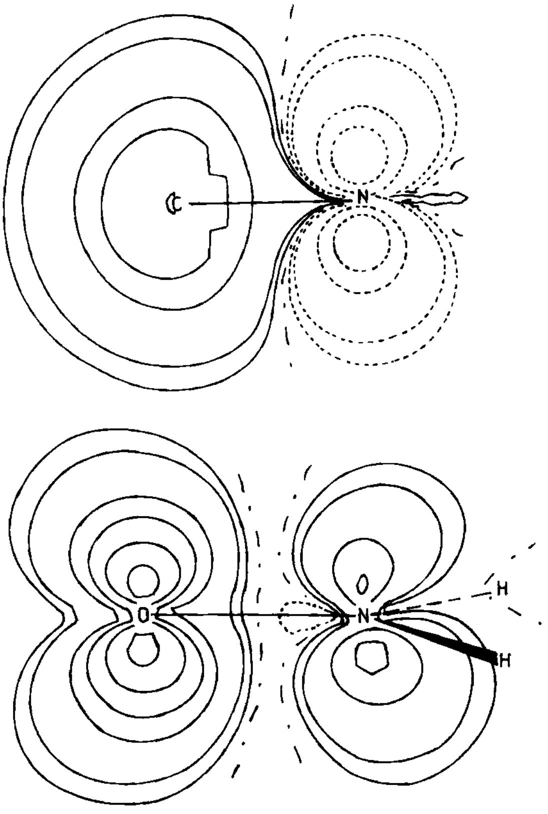


Fig. 8. Spin densities of $\dot{C}N$ and $H_2N\dot{O}$ radicals. Contours: (——) positive, (· · ·) negative, and (-----) zero values, respectively.

deed, as shown in Fig. 7, the H_α atoms of the ethyl radical lie in regions of negative spin density, and the H_β atoms, in regions of positive spin density. On the other hand, the σ-localized character of $\dot{C}N$ and the π-delocalized character of $H_2N\dot{O}$ are clearly demonstrated by the spin densities given in Fig. 8 (6-31G results).

b. The localized orbital approach (functional facet). We show here that the distribution of the centroids of charge of localized orbitals gives a picture of the electronic structure of chemical species that is very similar to those of Lewis and (or) Linnett. We will successively consider closed-shell and open-shell systems. All the results described below have been obtained at the SCF level with the minimal (STO-3G) or split-valence (4-31G or 6-31G) basis set, using the Boys localization procedure. More details about our methodology may be found in the papers cited throughout this section.

One knows that, for closed-shell systems, RHF and UHF methods give identical results: all the molecular orbitals are doubly occupied and then each centroid corresponds to a charge −2. The spatial distributions of the centroids of charge in some diatomic and polyatomic systems are, respectively, shown in Figs. 9 and 10. It is seen that they depend not only on the number of these centroids of charge but also on the number and

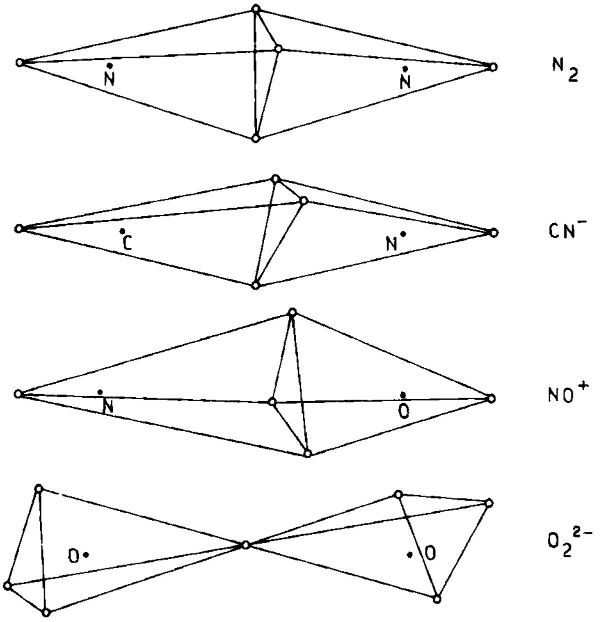


Fig. 9. Spatial distributions of centroids of charge (○) in some diatomic systems.

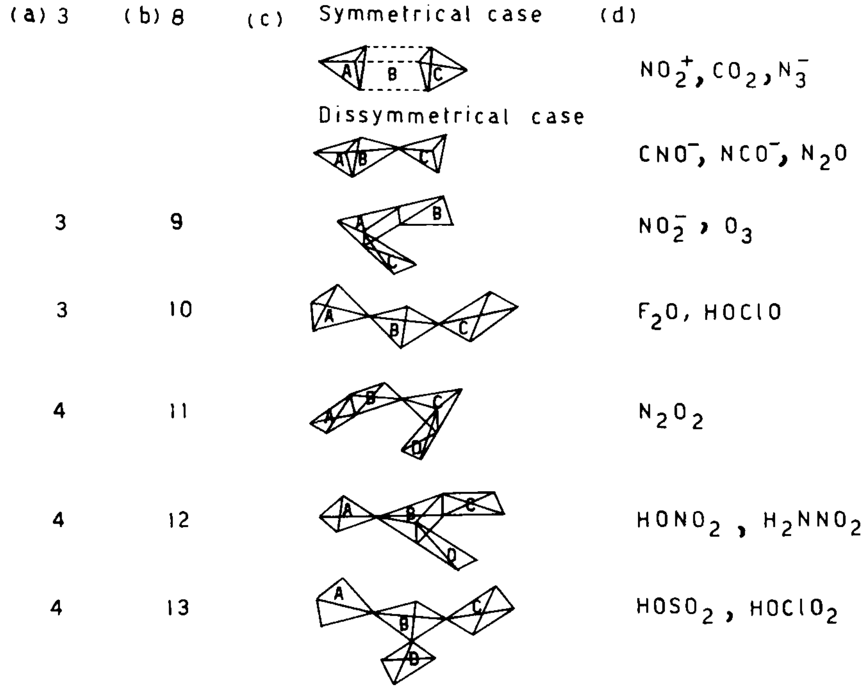


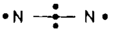
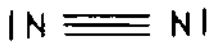
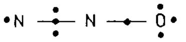
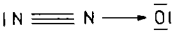
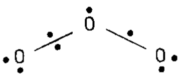
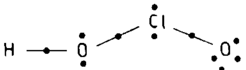
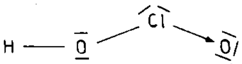
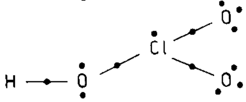
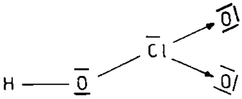
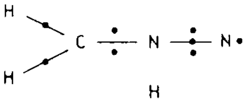
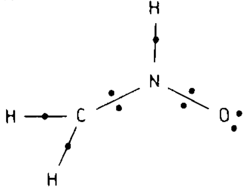
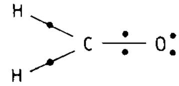
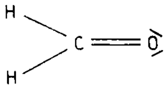
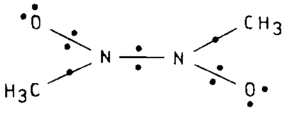
Fig. 10. Spatial distributions of the centroids of charge in some polyatomic systems. (a) Number of atomic cores. (b) Number of centroids of charge. (c) Spatial distribution; general case. (d) Typical examples.

nature of atomic cores (Leroy *et al.*, 1979). To simplify the description of the spatial distributions of the centroids of charge, we represent each of them by a black dot located in the same region of the molecular space. Moreover, we connect the bound atoms by straight lines, indicating the molecular skeleton. Such representations of previous results and other interesting ones are collected in Table IV with the corresponding available Lewis formulas.

It is seen that, every time a compound may be described by a unique Lewis formula, the latter corresponds quite well to the picture given by the centroid of charge distribution. Each dot plays the same role as a line in the Lewis formula, but we must emphasize that a dot is the centroid of charge of a doubly occupied localized orbital and not a localized shared electron pair. In other words, the presence of a centroid of charge in a given molecular region does not necessarily imply that two electrons are confined in the same region. This remark can be illustrated by two typical

TABLE IV

CENTROID OF CHARGE DISTRIBUTIONS AND LEWIS FORMULAS OF VARIOUS CHEMICAL SPECIES

Compound	Centroids of charge	Lewis formula
N_2		
O_2^{2-}		
N_2O		
O_3		—
$HOClO$		
$HOClO_2$		
H_2CN_2[a]		—
H_2CNHO[a]		—
H_2CO[a]		
$(H_3CNO)_2$		—

[a] Leroy *et al.* (1980).

examples, i.e., C_2 and N_3^-. The centroid of charge distributions in these compounds are given below:

C⁞C

·N⁞N⁞N·

These results do *not* mean that there are 8 electrons in the C_2 bond and 12 electrons around the central nitrogen atom in N_3^-.

For obtaining quantitative information about the mean number of electrons associated with bonds and lone pairs, we have to integrate electronic density in well-defined regions of the molecular space such as loges or pseudologes (see Section II,B,2,c, for discussion of *the pseudologe approach*). Such integrations have been performed for C_2 and N_3^- in domains defined by planes and half-spheres which correspond approximately to bond and lone-pair loges, respectively (Leroy *et al.*, 1979). One finds that the mean number of electrons in the C_2 bond loge is practically equal to 4, which corresponds to a "double bond," but in N_3^- there remain 10 electrons around the central nitrogen atom. The physical meaning of the centroids of charge will be examined on analyzing the pseudologe approach.

For open-shell systems, the Boys localization procedure leads to two sets of centroids, of α and β type, respectively, corresponding each to a charge -1. Their distributions in some diatomic species are given in Fig. 11. It is seen that the spatial arrangement of centroids of a given set ($\alpha \equiv \times$ or $\beta \equiv \circ$) depends on their number. Moreover, the distances between α (or β) centroids are larger than those between centroids of different types. On the whole, the picture provided by the localization procedure is identical to the corresponding Linnett structure. However, our symbols (× or ○) represent centroids of charge of singly occupied (α or β) molecular orbitals and not localized α or β electrons as in Linnett's formulas.

Using a simplified representation of centroid of charge distributions, one obtains the pictures collected in Table V, for a series of model free radicals. When two centroids of different types (α and β) are near one to the other, we adopt the Linnett notation, i.e., a line, but we do not distinguish between spatial and nonspatial pairs. Moreover, centroids of the CH, NH, or OH bond are not always indicated.

Analyzed together with spin densities and Mulliken spin populations, the results of Table V allow us to determine the character of each type of free radical (Leroy, 1983b). To illustrate this, we consider two typical examples: $H\dot{C}O$ and $HO\dot{O}$. The properties of these species are shown in Figs. 12 and 13, respectively.

In $H\dot{C}O$, the centroid of charge which appears alone near the carbon atom is that of a σ-localized orbital (of α type: ϕ_σ^α). All the other centroids

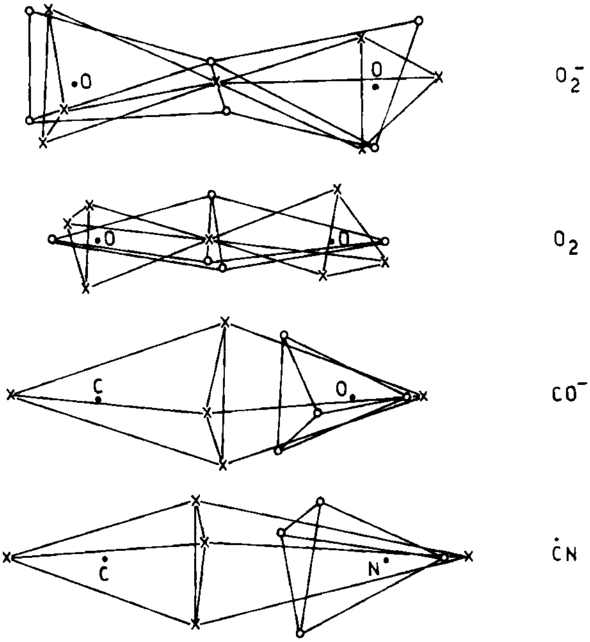
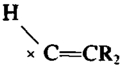
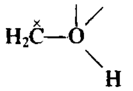
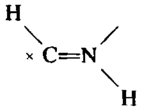
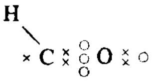


Fig. 11. Spatial distributions of centroids of charge in some diatomic open-shell systems. Symbols: × and ○ represent centroids of charge of α and β type, respectively.

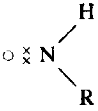
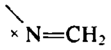
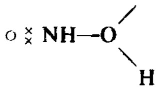
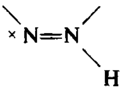
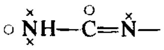
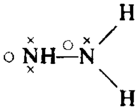
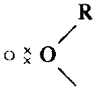
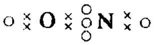
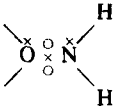
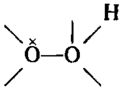
TABLE V

CENTROID OF CHARGE DISTRIBUTIONS OF VARIOUS TYPES OF FREE RADICALS, $\overset{\times}{C}(N,O)X(Y,Z)$[a]

C	$\overset{\times}{C}XYZ$	$\overset{\times}{C}X{=}Y$	$\overset{\times}{C}{\equiv}X$
	Alkyls	**Vinyls**	**Ethynyls**
	$H_2\overset{\times}{C}—R$		$\times\ C{\equiv}CH$
	Substituted species	**Iminovinyls**	**Cyanyl**
			$\times\ C{\equiv}N—$
	$H_2\overset{\times}{C}\overset{\circ}{—}\overset{\times}{N}H_2$	**Acyls**	
	$H_2\overset{\times}{C}—\overset{\circ}{C}{=}\overset{\times}{N}—$		

(continued)

TABLE V (*Continued*)

N	$\overset{\times}{N}XY$	$\overset{\times}{N}{=}Y$
	Aminyls	**Iminyls**
		
	Substituted species	**Diimidyls**
		
		
	Hydrazyls	
		
O	$\overset{\times}{O}X$	$\overset{\times}{O}{=}X$
	Hydroxyls	**Nitrogen oxide**
		
	Nitroxides	
		
	Peroxides	
		

[a] Fully optimized SCF-6-31G results (Leroy *et al.*, 1983a).

are more or less paired. Moreover, the sum of the π spin populations (densities) is equal to zero. Thus it follows that formyl may be considered as a σ radical. This is confirmed by the important values of the spin density near the carbon atom in the molecular plane. However, as shown by the spin density map in the plane perpendicular to the molecular skele-

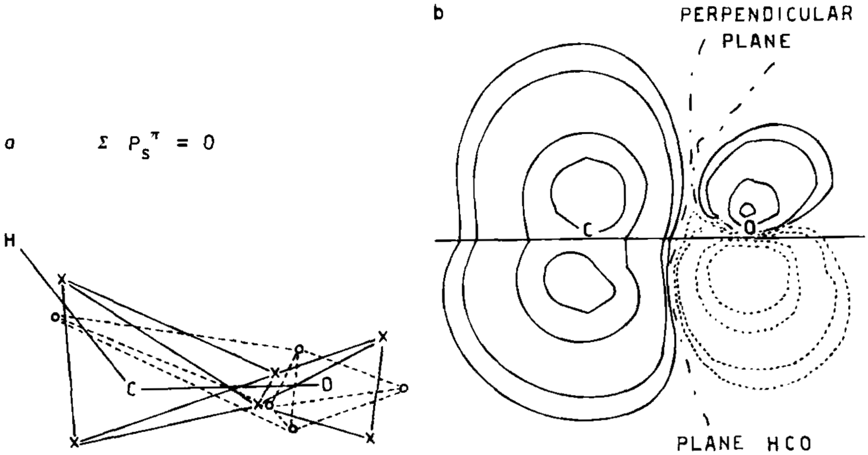


Fig. 12. Electronic properties of the formyl radical. (a) Charge centroid distribution. (b) Spin density.

ton and containing the C—O bond axis, H$\dot{\mathrm{C}}$O is not a σ-localized species, as we could believe by considering only the previous results. Indeed, one observes a nonnegligible spin delocalization which can be qualitatively explained by the mechanisms of spin polarization and conjugation.

In HO$\dot{\mathrm{O}}$ the centroid of charge appearing alone, close to the terminal oxygen atom, corresponds to a π-localized orbital (of α type: ϕ_π^α). Here again the other centroids are approximately paired. Furthermore, the sum of the π spin populations is equal to 1. Then hydroperoxide is a π radical.

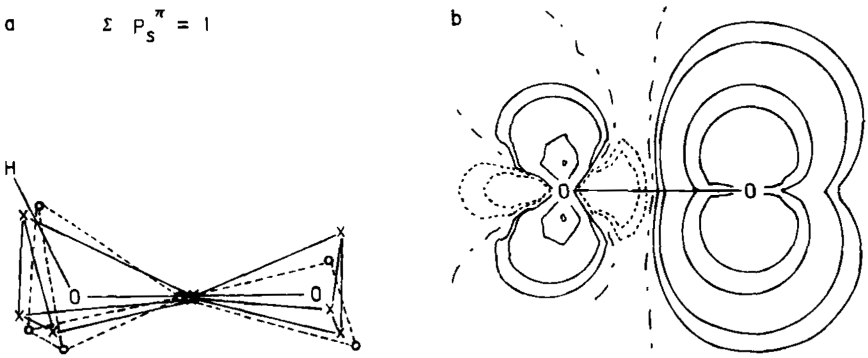


Fig. 13. Electronic properties of the hydroperoxide radical. (a) Charge centroid distribution. (b) Spin density.

TABLE VI

ELECTRONIC PROPERTIES OF MODEL FREE RADICALS

Radicals	Type	Character
Alkyls	π	Localized, atom centered
$H_2\dot{C}$ d[a]	pseudo π	Delocalized
$H_2\dot{C}$ c[a]	π	Delocalized
Vinyls	σ	Localized, atom centered
Iminovinyls	σ	Little delocalized
Acyls	σ	Delocalized
Ethynyls	σ	Localized, atom centered
Cyanyl	σ	Localized, atom centered
Aminyls	π	Localized, atom centered
$H\dot{N}$ d[a]	π	Delocalized
$H\dot{N}$ c[a]	π	Delocalized
Hydrazyls	π	Delocalized
Iminyls	σ	Localized, atom centered
Diimidyls	σ	Localized, atom centered
Hydroxyls	π	Localized, atom centered
Nitroxides	π	Delocalized
Peroxides	π	Delocalized

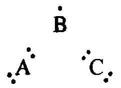
[a] Symbols d and c mean π donor and captor (substituents), respectively.

The spin density not only confirms this conclusion but also shows that $HO\dot{O}$ is a delocalized species. All the results obtained by this approach are summarized in Table VI. We shall show in Section III that the stability of free radicals is closely related to their electronic properties reported in this table.

In conclusion, the Boys localization procedure may be considered as the mathematification of the qualitative Lewis and Linnett theories. As pointed out, in this perspective a formal signification of the symbols used by these authors can be proposed: these represent not localized electrons but centroids of charge of localized orbitals. Within this interpretation, the former theories agree much better with the ideas of quantum mechanics such as the wave character of electrons that prevents their localization. Moreover, the results obtained by the Boys procedure allow us to predict the Lewis and (or) Linnett structures of many chemical species without performing explicit calculations. For example, linear and bent 1,3-dipoles are described by the following general formulas:

$$:A:B\vdots C\cdot \qquad \text{for linear species}$$

and



for bent species

whatever A, B, and C may be, in each class of dipoles. However, the physical interpretation of Lewis and Linnett's symbols and therefore their fundamental justification remain to be given. This is the problem we shall now envisage.

c. The pseudologe approach (partitioning facet). The Lewis formula of a chemical species suggests that electrons are distributed two by two in definite regions of the molecular space (core, lone-pair, and bond regions). We may wonder whether such partition of a molecule can be justified by quantum mechanics. This question has been examined first by Daudel (1953) in his well-known loge theory and also by Bader and Beddall (1972) using their virial method.

The loge theory is a procedure to extract information on the localizability of electrons in a chemical system from the wave function of this system. It has been shown (Daudel *et al.*, 1983, and references therein) that the molecular space of small species such as LiH^+, LiH, BeH, BH, and BeH_2 can be actually partitioned into fragments predominantly associated with cores, bonds, and lone pairs. These fragments (the so-called loges) contain also a definite number of electrons corresponding to the leading electronic event. For the "best" loges:

1. The virial theorem is satisfied.
2. The missing information is a minimum.
3. The fluctuation in the average population is a minimum.
4. The properties are transferable from one molecule to another.
5. The electronic correlation is a maximum in the loge and a minimum between two different loges.

These five criteria give a real physical meaning to the concept of chemical bond.

So, the loge theory provides the best justification of Lewis ideas. For example, it is found that the six electrons of the BH molecule are distributed two by two in core, bond, and lone-pair loges. This result corresponds to the classical (Lewis) formula:

$$|\,B—H$$

The loge theory leads also to a unified description of the various types of chemical bonds (Daudel and Veillard, 1970).

The extent to which individual electron pairs are localized in distinct spatial regions has been carefully analyzed by Bader and Stephens (1975) using the minimum fluctuation criterion. These authors arrive at the conclusion that "the model of spatially localized pairs is appropriate for LiH, BeH_2, BH_3, and BH_4^-, it is borderline for CH_4, but in NH_3, OH_2, FH, Ne, N_2, and F_2, the motions of the valence electrons are so strongly intercorrelated, the localized pair model ceases to afford a suitable description." Moreover, their results provide "no physical basis for the view that there are two separately localized pairs of nonbonded electrons in H_2O." This clearly shows the limit of the Lewis electron pair concept which otherwise has practically disappeared in Linnett's theory.

The loge partitioning theory is not easy to apply to large molecular systems whatever the chosen criterion may be. It is the reason why, following Daudel's idea, we have proposed (Leroy and Peeters, 1975) a much simpler but obviously less rigorous method to partition a molecular space into core, bond, and lone-pair fragments. It is based on the intuitive assumption that the regions in which molecular orbitals are best localized are approximate loges. This is the basic idea of the pseudologe approach. We call pseudologe a fragment of the molecular space in which the contribution of a given localized orbital is much larger than that of any other LMO. The frontiers of these pseudologes are simply the collection of points in which intersect the LMO's isodensity contours of the same value.

The pseudologe partitioning of a series of diatomic and polyatomic compounds has been performed and, for each fragment Ω, the following properties have been calculated:

1. The volume:

$$V(\Omega) = \int_\Omega dv \tag{57}$$

2. The average number of electrons:

$$\bar{N}(\Omega) = \int_\Omega \rho(M)\, dv \tag{58}$$

3. The position of the center of charge (first moment):

$$\langle u\rangle(\Omega) = \frac{1}{\bar{N}(\Omega)} \int u\rho(M)\, dv; \qquad u = x, y, z \tag{59}$$

4. The dispersion of the electronic charge (second moment):

$$\langle uv\rangle(\Omega) = \frac{1}{\bar{N}(\Omega)} \int uv\rho(M)\, dv; \qquad u, v = x, y, z \tag{60}$$

Another way to define this dispersion is to consider the expectation value of the quadratic moment operator with its origin at the centroid of charge:

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle \tag{61}$$

This quantity is often assumed to be a measure of the size of the corresponding domain (in this case, the pseudologe under consideration).

5. For some compounds, the fluctuation in $\bar{N}(\Omega)$ has also been calculated:

$$\Lambda(\bar{N}, \Omega) = \bar{N}^2(\Omega) - [\bar{N}(\Omega)]^2 \tag{62}$$

Let us now analyze the preliminary results obtained by the pseudologe approach. As shown previously, in the case of the BH molecule, the frontiers of pseudologes are quite close to those of exact loges (Daudel *et al.*, 1977). We show below that other properties of loges and pseudologes are very similar. In calculating $V(\Omega)$ and $N(\Omega)$, we do not consider individual lone-pair pseudologes but a unique lone-pair domain delimited by the external isodensity surface previously defined and the nearby core and bond pseudologes. In the same way, we consider only one CC bond pseudologe in C_2H_4 and C_2H_2. Moreover, in order to avoid the error due to the truncation of the "molecular volume," the mean electronic population of the valence pseudologes is systematically normalized to the total number of valence electrons, the population of each core fragment being conventionally taken equal to two.

The volume, the mean number of electrons, and (when calculated) the fluctuation of core pseudologes (PL) of the chosen molecules are collected in Table VII. They are compared with the corresponding available results obtained by a loge (L) partitioning procedure (Bader and Stephens, 1975). For each property, one observes a satisfactory agreement between the two series of values. Indeed they are of the same order of magnitude and exhibit the same trends. As shown in Tables VIII and IX, respectively, the properties of bond and lone-pair pseudologes are also similar to those of the corresponding loges, except in the case of the HF molecule.

From the results in Tables VII–IX, we may conclude that *pseudologes are approximate loges*. Moreover, it is seen that the properties of each type of pseudologe are transferable from one molecule to another of the same series. Some other preliminary conclusions can also be drawn:

1. The mean number of electrons in any pseudologe is never very far from two or a multiple of two, but this is not an indication of electron pairing.

TABLE VII

PROPERTIES OF CORE LOGES[a] AND PSEUDOLOGES (VOLUMES IN ATOMIC UNITS)

XH_n	V(PL)			$\bar{N}$(PL)				
XH_mYH_n	X	Y	V(L)	X[b]	Y[b]	$\bar{N}$(L)	Λ^c(PL)	Λ(L)
LiH	10.40	—	11.99	2.0	—	1.999	—	0.091
BeH_2	3.09	—	3.59	2.0	—	2.012	—	0.137
BH	1.25	—	—	2.0	—	—	—	—
CH_4	0.65	—	0.62	2.0	—	2.005	0.219	0.239
NH_3	0.36	—	0.33	2.0	—	2.002	0.233	0.276
H_2O	0.22	—	0.20	2.0	—	2.001	0.260	0.310
HF	0.14	—	0.11	2.0	—	1.966	—	0.345
C_2H_2	0.63	0.63	—	2.0	2.0	—	—	—
C_2H_4	0.63	0.63	—	2.0	2.0	—	—	—
C_2H_6	0.65	0.65	—	2.0	2.0	—	—	—
CH_3NH_2	0.65	0.36	—	2.0	2.0	—	—	—
CH_3OH	0.65	0.22	—	2.0	2.0	—	—	—
CH_3F	0.66	0.14	—	2.0	2.0	—	—	—
BH_3NH_3	1.25	0.37	—	2.0	2.0	—	—	—

[a] Bader and Stephens (1975).
[b] Assumed value.
[c] Tihange (1983).

TABLE VIII

PROPERTIES OF BOND LOGES[a] AND PSEUDOLOGES (VOLUMES IN ATOMIC UNITS)

XH_n	V(PL)			$\bar{N}$(PL)			$\bar{N}$(L)	Λ^b(PL)	Λ(L)
XH_mYH_n	XH	YH	XY	XH	YH	XY	XH	XH	XH
LiH	209.02	—	—	2.000	—	—	2.001	—	0.091
BeH_2	136.36	—	—	2.000	—	—	1.994	—	0.144
BH	93.43	—	—	1.999	—	—	—	—	—
CH_4	63.79	—	—	2.000	—	—	1.999	0.630	0.622
NH_3	54.86	—	—	1.988	—	—	1.997	0.734	0.771
H_2O	50.81	—	—	1.937	—	—	1.987	0.795	0.870
HF	50.59	—	—	1.876	—	—	2.037	—	0.956
C_2H_2	76.14	76.14	131.05	2.145	2.145	5.710	—	—	—
C_2H_4	67.83	67.83	70.46	2.052	2.052	3.790	—	—	—
C_2H_6	63.45	63.45	19.06	2.004	2.004	1.971	—	—	—
CH_3NH_2	64.14	54.68	15.75	2.010	2.004	1.966	—	—	—
CH_3OH	65.14	50.60	13.74	2.013	1.959	1.902	—	—	—
CH_3F	66.50	—	13.87	2.011	—	1.829	—	—	—
BH_3NH_3	78.52	53.52	19.97	1.998	2.000	2.011	—	—	—

[a] Bader and Stephens (1975).
[b] Tihange (1983).

TABLE IX

PROPERTIES OF LONE-PAIR LOGES[a] AND PSEUDOLOGES (VOLUMES IN ATOMIC UNITS)

XH_n XH_mYH_n	$V(PL)$ X, Y	$\bar{N}(PL)$ X, Y	$\bar{N}(L)$ X	$\Lambda^b(PL)$ X, Y	$\Lambda(L)$ X
BH	107.84	2.001	—	—	—
NH_3	33.43	2.036	2.005	0.835	0.899
H_2O	46.06	4.126	4.010	1.210	0.968
HF	52.78	6.124	5.997	—	1.011
CH_3NH_2	32.38	2.003	—	—	—
CH_3OH	45.98	4.100	—	—	—
CH_3F	53.87	6.139	—	—	—

[a,b] See footnotes to Table VIII.

2. The volume of a lone-pair pseudologe is systematically smaller than the volume of the nearby bond pseudologe (except in the BH molecule).

3. The variation of the spherical quadratic moment operator of a given type of pseudologe in a series of compounds is not always parallel to that of the corresponding volume (see Table X).

TABLE X

EXPECTATION VALUE OF THE SPHERICAL QUADRATIC MOMENT OPERATOR OF PSEUDOLOGES (IN ATOMIC UNITS)

XH_n XH_mYH_n	Core		Bond			Lone pair(s) X, Y
	X	Y	XH	YH	XY	
LiH	0.618	—	1.956	—	—	—
BeH_2	0.439	—	1.665	—	—	—
BH	0.336	—	1.440	—	—	1.569
CH_4	0.279	—	1.286	—	—	—
NH_3	0.234	—	1.190	—	—	1.027
H_2O	0.201	—	1.143	—	—	1.112
HF	0.176	—	1.077	—	—	1.039
C_2H_2	0.277	0.277	1.344	1.344	1.654	—
C_2H_4	0.278	0.278	1.306	1.306	1.519	—
C_2H_6	0.279	0.279	1.288	1.288	1.144	—
CH_3NH_2	0.282	0.234	1.290	1.196	1.071	1.025
CH_3OH	0.279	0.201	1.293	1.126	1.006	1.115
CH_3F	0.279	0.176	1.300	—	0.965	1.045
BH_3NH_3	0.341	0.235	1.393	1.201	1.055	—

4. The center of charge of a pseudologe is never very far from the centroid of charge of the corresponding localized molecular orbital (see Table XI).

Thus, in first approximation, *in closed-shell systems, the LMO's centroids of charge can be identified with centers of charge of (pseudo)loges.* So, we find a physical interpretation of Lewis symbols. They no longer

TABLE XI

FIRST MOMENT OF PSEUDOLOGES AND CORRESPONDING LMOs[a]

	Core		Bond			Lone pair(s)
XH_n XH_mYH_n	X d(XC)	Y d(YC)	XH d(XC)	YH d(YC)	XY d(XC)	X, Y d(X, YC)
LiH	0.011	—	2.479	—	—	—
	(0.007)		(2.469)			
BeH_2	0.000	—	1.991	—	—	—
	(0.000)		(1.979)			
BH	0.000	—	1.841	—	—	0.866
	(0.003)		(1.768)			(0.794)
CH_4	0.000	—	1.569	—	—	—
	(0.000)		(1.412)			
NH_3	0.000	—	1.408	—	—	0.893
	(0.002)		(1.223)			(0.673)
H_2O	0.000	—	1.303	—	—	0.397
	(0.001)		(1.089)			(0.291)
HF	0.000	—	1.220	—	—	0.184
	(0.000)		(0.984)			(0.124)
C_2H_2	0.000	0.000	1.413	1.413	1.138	—
	(0.000)	(0.000)	(1.354)	(1.354)	(1.138)	
C_2H_4	0.000	0.000	1.529	1.529	1.259	—
	(0.000)	(0.000)	(1.406)	(1.406)	(1.259)	
C_2H_6	0.000	0.000	1.573	1.573	1.449	—
	(0.000)	(0.000)	(1.417)	(1.417)	(1.449)	
CH_3NH_2	0.000	0.000	1.566	1.404	1.487	0.894
	(0.000)	(0.003)	(1.418)	(1.222)	(1.528)	(0.647)
CH_3OH	0.000	0.000	1.564	1.297	1.478	0.400
	(0.000)	(0.003)	(1.417)	(1.084)	(1.566)	(0.282)
CH_3F	0.000	0.000	1.568	—	1.466	0.175
	(0.000)	(0.000)	(1.431)		(1.596)	(0.102)
BH_3NH_3	0.000	0.000	1.850	1.392	1.912	—
	(0.000)	(0.000)	(1.742)	(1.196)	(2.028)	

[a] LMO values in parentheses; distances atom center (centroid) of charge in atomic units.

represent localized electron pairs but centers of charge of loges, reasonably well represented by the LMO's centroids of charge. Within this interpretation, no assumption is made concerning the pairing of electrons, although each centroid strictly corresponds to a charge −2. Then, nowadays, the Boys localization procedure appears to be the simplest quantitative approach to the electronic structure of closed-shell systems (molecules or supermolecules).

No pseudologe partitioning of open-shell systems has yet been performed. Therefore, we cannot propose any quantitative physical interpretation of the centroids of charge of singly occupied LMOs that we have identified with Linnett's symbols. However, as shown before, the correlation between the spin density function of an open-shell system and its centroid of charge distribution leads us to assume a certain correspondence between each centroid and an electron of the same spin. In other words, the mean number of electrons in a given region (provisionally not precisely defined) of the molecular space would be approximately equal to the number of centroids in the same region. Other experimental facts qualitatively support this assumption. For example, the centroid of charge distributions (or Linnett's structure) of O_2 and its positive and negative ions suggest the same order of stability of these species as the Herzberg shell model, which is experimentally confirmed. Thus, for want of something better, we shall also use the Boys localization procedure for determining the electronic structure of open-shell systems. So, in our opinion, the localized orbital approach may be considered as the achievement of the (Lewis and Linnett) electronic theory of valence. In the future, it remains to integrate the various facets of the concept of bond in a unified quantum theory of valence.

III. The Thermodynamical Properties of Chemical Species

A. Heats of Formation and Atomization

1. *Introduction*

Heats of reaction may be obtained from molar enthalpies by using the equation:

$$\Delta H(T) = \sum_i k_i N_i H_i(T) \tag{63}$$

or, referring to standard state (pressure of 1 atm), at 298.15 K:

$$\Delta H^0(298.15) = \sum_i k_i N_i H_i^0(298.15) \tag{64}$$

Molar enthalpies are given by Eq. (22), which shows that, in principle, heats of reaction can be theoretically calculated at any temperature from the total energies of the constituents and the frequencies of their normal modes of vibration. However, it is well known that heats of reaction obtained at the SCF level are not very accurate due to correlation errors on total energies which only accidentally cancel.

Some years ago, Pople and co-workers (Hehre *et al.*, 1970) introduced the interesting concept of isodesmic reaction. By definition, this is a reaction in which all the bonds are conserved (in number and nature). The corresponding theoretical heat of reaction is generally reliable due to approximate cancellation of correlation errors. Moreover, in that case, ZPE and thermal corrections are often negligible. Thus, we may write:

$$\Delta E^0(0) = \sum_i k_i N_i u_i^0(0) \simeq \Delta H^0(298.15) \qquad (65)$$

This allows us to use a semiempirical procedure for estimating the heat of formation of any chemical species. For that purpose, we introduce the experimental heats of formation of reference compounds in the following equation:

$$\Delta E^0(0) \simeq \sum_i k_i N_i [\Delta H_f^0(298.15)]_i \qquad (66)$$

Furthermore, the heat of atomization of the species under consideration can be determined from the experimental heats of formation of gaseous atoms, using the equation:

$$\Delta H_a^0(298.15) = \sum_a [\Delta H_f^0(298.15)]_a - \Delta H_f^0(298.15) \qquad (67)$$

To illustrate this procedure, we estimate below the heats of formation and atomization of the $\dot{C}N$ radical. We choose the isodesmic reaction:

$$\dot{C}N + CH_4 \rightarrow HCN + \dot{C}H_3$$

Using the data of Table XII, one obtains:

$$\Delta E^0(0) = -19.14 \quad \text{kcal mol}^{-1} \qquad (68)$$

which compares quite well with the experimental value at 0 K: −19.95 kcal mol^{-1}. On the other hand, thermal and ZPE corrections are actually very small (0.96 kcal mol^{-1}). Thus we may write according to Eq. (66):

$$\Delta E^0(0) = \Delta H_f^0(HCN) + \Delta H_f^0(\dot{C}H_3) - \Delta H_f^0(CH_4) - x \qquad (69)$$

and we find:

$$x = \Delta H_f^0(\dot{C}N) = 104.15 \text{ kcal mol}^{-1}(298.15\text{ K}) \qquad (70)$$

which is in perfect agreement with the corresponding experimental value. Finally, $\Delta H_a^0(\dot{C}N)$ is readily obtained from the heats of formation of gas-

TABLE XII

6-31G TOTAL ENERGIES, ZPE AND THERMAL CORRECTIONS, AND EXPERIMENTAL HEATS OF FORMATION OF $\dot{\mathrm{C}}$N RADICAL AND REFERENCE COMPOUNDS

Species	$u^0(0)$ (a.u.)	Corrections(298.15) (kcal mol^{-1})	ΔH_f^0(298.15) (kcal mol^{-1})
$\dot{C}N$	−92.16324[a]	5.03[e]	104 ± 2.5[g]
HCN	−92.82763[b]	11.97[f]	32.30[h]
CH_4	−40.18055[c]	29.48[f]	−17.89[i]
C_2H_6	−79.19748[c]	48.04[f]	−20.24[i]
$\dot{C}H_3$	−39.54666[d]	23.50[d]	34.82[g]

[a] Sana and Leroy (1981).
[b] Hehre *et al.* (1972).
[c] Radom *et al.* (1971).
[d] Sana (1981b).
[e] Moffat and Knowles (1969).
[f] Herzberg (1945).
[g] Stull and Prophet (1971).
[h] Benson *et al.* (1969).
[i] Cox and Pilcher (1970).

eous atoms (Cox and Pilcher, 1970):

$$\Delta H_a^0(\dot{C}N) = 179.75 \text{ kcal mol}^{-1}(298.15 \text{ K}) \tag{71}$$

It is noticeable that the choice of the isodesmic reaction depends on the species under consideration. This choice is often made *a posteriori* on the basis of the accuracy of the results obtained for similar compounds. In this work, we have adopted the following isodesmic processes for the various types of compounds.

1. Carbon-centered radicals:

$$\dot{C}XYZ + C_2H_6 \rightarrow HCXYZ + \dot{C}_2H_5$$

2. Carbocations:

$$\overset{+}{C}H_2X + C_2H_6 \rightarrow CH_3X + \overset{+}{C}_2H_5$$

$$\overset{+}{C}HX_2 + CH_3X \rightarrow CH_2X_2 + \overset{+}{C}H_2X$$

$$\overset{+}{C}X_3 + CH_2X_2 \rightarrow CHX_3 + \overset{+}{C}HX_2$$

3. Nitrogen-centered radicals; for example:

$$\dot{N}XY + N_2H_4 \rightarrow HNXY + \dot{N}_2H_3$$

4. Molecules: bond separation reactions (Hehre *et al.*, 1970).

Except as otherwise specified, all the results described in this subsection have been obtained by *ab initio* SCF calculations, at the 4-31G level. The geometry of each species has been fully optimized using the gradient techniques of the Gaussian series of programs (Binkley *et al.*, 1981).

2. *Theoretical Results*

Heats of formation of a series of carbon-centered radicals ($R^{\cdot}$), parent molecules (RH), dimers (R—R), and corresponding carbocations (R^+) are collected in Table XIII. They have been obtained using the semiempirical procedure described earlier. More details about the calculations may be found elsewhere (Leroy and Peeters, 1981; Peeters *et al.*, 1983) or will be published later on (particularly those concerning the dimers and the carbocations). Experimental heats of formation of the various species are also given in the Table XIII. Except in the case of $\dot{C}F_3$, the agreement between theory and experiment is satisfactory for radicals, parent molecules, and dimers. It may seem less good in the case of carbocations, especially the fluoro derivatives, but we must remember that the experimental heats of formation of carbocations are always obtained by indirect measurements (such as of C—H bond dissociation energy and ionization potential of the corresponding radical), which are not always very precise. For example, three different values of $\Delta H_f^0(CH_3NHC^+H_2)$ may be found in the literature: 166 (Griller and Lossing, 1981), 160.5 (Solka and Russell, 1974), and 174.1 (Taft *et al.*, 1965) kcal mol^{-1}. The theoretical value (162.5 kcal mol^{-1}) suggests to the experimentalists a need to reexamine the validity and (or) the interpretation of their results.

We are actually convinced that semiempirical heats of formation of unknown species are accurate enough to allow a significant prediction of thermochemical data (such as bond dissociation energies) and adiabatic ionization potentials of new free radicals. For example, the semiempirical N—H bond dissociation energies for a series of aminyl radicals have been calculated at the 4-31G level (Leroy *et al.*, 1983b). These are given in Table XIV. Only a few of them have been experimentally determined, and these are in satisfactory agreement with the corresponding theoretical values. Finally, recent 6-31G results concerning small free radicals (Leroy *et al.*, 1983c) are given in Table XV. Some of them have been obtained

TABLE XIII

HEATS OF FORMATION OF A SERIES OF CARBON-CENTERED RADICALS ($R^{\cdot}$), PARENT MOLECULES (RH), DIMERS (R—R), AND CORRESPONDING CARBOCATIONS (R^+) (IN KCAL MOL^{-1})

R	$R^{\cdot}$		RH		R—R		R^+	
	Theo.	Exp.	Theo.	Exp.	Theo.[a]	Exp.	Theo.	Exp.
$CH(CH_3)_2$	20.77	19.2[b]	−23.65	−24.83[i]	−42.02	−42.61[i]	188.63	189.3[p]
$C(CH_3)_3$	11.02	9.4[b]	−27.64	−32.41[i]	−49.53	−53.83[i]	164.06	163.9[p]
CH_2CHCH_2	34.18	39.4[c]	5.86	4.88[i]	—	—	216.00	226.9[p]
CH_2OH	−2.80	−4.2[d]	—	−48.07[i]	−91.85	−92.70[l]	171.12	169.0[q]
$CH(OH)_2$	−45.07	—	−93.70	−93.50[e]	−181.82	—	105.05	97.0[r]
CH_2OCH_3	2.16	−2.0[e]	−40.82	−43.99	—	—	160.90	158.0[q]
CH_2CN	56.49	58.5[f]	17.30	17.62[j]	47.59	50.12[m]	291.54	294.8[s]
$CH(CN)_2$	90.91	—	62.08	63.50[i]	139.78	—	346.46	—
CH_2NH_2	35.66	36.0[g]	—	−5.50[i]	−2.02	−4.07[n]	170.90	178.0[t]
CH_2NHCH_3	38.13	30.0[g]	−2.23	−4.43[i]	—	—	162.50	166.0[t]
$CH_2N(CH_3)_2$	36.89	26[g], 32[v]	0.09	−5.67[i]	—	—	154.20	158.0[t]
CH_2F	−7.00	−7.9[h]	—	−56.80[k]	−103.88	—	208.11	199.5[u]
CHF_2	−61.53	−58.3[h]	−105.59	−108.13[i]	−213.84	—	166.07	142.0[u]
CF_3	−111.76	−112.0[d]	−158.46	−166.30[i]	−324.72	−320.9[o]	133.52	93.8[u]
H_2NCHCN	56.90	—	27.94	—	—	—	226.56	—
HOCHCN	21.53	—	−11.48	—	−20.63	—	226.53	—
FCHCN	20.68	—	−16.84	—	—	—	260.89	—

[a] The total energies of the dimers were calculated at STO-3G level (Leroy *et al.*, 1983d).
[b] Castelhano and Griller (1982).
[c] Rossi and Golden (1979).
[d] O'Neal and Benson (1973).
[e] Benson (1976).
[f] King and Goddard (1975).
[g] Griller and Lossing (1981).
[h] Pickard and Rodgers (1983).
[i] Cox and Pilcher (1970).
[j] An and Mänsson (1983).
[k] Rodgers *et al.* (1974).
[l] Gardner and Hussain (1972).
[m] Rapport *et al.* (1971).
[n] Good and Moore (1970).
[o] Chen *et al.* (1975).
[p] $\Delta H_f(R^+) = \Delta H_f(R^{\cdot}) + IP(R^{\cdot})$ (Houle and Beauchamp, 1978, 1979).
[q] Lossing (1977).
[r] Yam Dagni and Kebarle (1976).
[s] Pottie and Lossing (1961).
[t] Lossing *et al.* (1981).
[u] Lias and Ausloos (1977).
[v] Loguinov *et al.* (1981).

TABLE XIV

Heats of Formation and N—H Bond Dissociation Energies for a Series of Aminyl Radicals (in kcal mol^{-1})[a]

Radical	$\Delta H_f^0(298.15)$	$BDE(N—H)(298.15)$
$\dot{N}(CN)_2$	130.00	90.51
$\dot{N}H_2$	38.66	101.73
	(42.0)[b]	(105.1)
$\dot{N}HCH_3$	38.12	95.12
	(39.3)[c]	(96.9)
$\dot{N}(CH_3)_2$	36.49	93.02
	(37.4)[c]	(94.0)
$\dot{N}HNO_2$	48.31	96.20
$\dot{N}(OH)(CN)$	71.88	72.73
$\dot{N}(CH_3)(CN)$	75.61	91.47
$\dot{N}HCN$	76.86	96.42
$\dot{N}(OH)(NO_2)$	33.85	66.95
$\dot{N}HF$	22.90	86.50
$\dot{N}(NH_2)(CN)$	95.98	82.03
$HO\dot{N}H$	23.03	84.13
$\dot{N}HNH_2$	53.32	82.62
	(46.56[d]–56.02)[e]	(75.86–85.32)
$\dot{N}F_2$	5.86	73.56
	(7.8)[f]	(75.5)
$\dot{N}(OH)_2$	10.49	76.23
$\dot{N}(NH_2)_2$	70.99	74.03

[a] Experimental results are given in parentheses.
[b] Demissy and Lesclaux (1980).
[c] O'Neal and Benson (1973).
[d] Foner and Hudson (1958).
[e] Fisher and Heath (1965).
[f] Evans and Tschuikow-Roux (1978).

using the following isoelectronic processes instead of isodesmic reactions:

$$H\dot{C}O + NH_2OH \rightarrow CH_3OH + \dot{N}O$$

$$NH_2\dot{N}H + CH_3OH \rightarrow NH_2NH_2 + \dot{C}H_2OH$$

$$CH_3\dot{N}H + C_2H_6 \rightarrow CH_3NH_2 + \dot{C}_2H_5$$

$$NH_2\dot{O} + CH_3NH_2 \rightarrow NH_2OH + CH_3\dot{N}H$$

$$HO\dot{O} + CH_3NH_2 \rightarrow HOOH + CH_3\dot{N}H$$

TABLE XV

HEATS OF FORMATION OF SOME SMALL FREE RADICALS (IN KCAL MOL^{-1})

Radical	Semiempirical $\Delta H_f^0(298.15)$	Experimental $\Delta H_f^0(298.15)$
$\dot{C}H_3$	33.05	34.4[a]
$CH\dot{C}$	125.63	124.4[b]
$CH_2\dot{C}H$	67.36	63.4[c]
$\dot{C}N$	106.90	104.0[d]
$\dot{C}H_2NH_2$	37.91	36.0[e]
$\dot{C}_2H_5$	29.35	28.0[a]
$\dot{C}HNH$	74.85	—
$\dot{N}H_2$	43.78	42.0[f]
$\dot{N}O$	23.12	21.6[g]
$CH_2\dot{N}$	53.27	—
$NH\dot{N}$	63.53	58.4[h]
$HO\dot{N}H$	28.15	—
$NH_2\dot{N}H$	51.47	46.56[i]–56.02[j]
$CH_3\dot{N}H$	41.28	45.0[g]
$NH_2\dot{O}$	15.60	—
$HO\dot{O}$	1.13	3.0[k]

[a] Castelhano and Griller (1982).

[b] Ono and Ng (1981).

[c] Ayranci and Back (1983).

[d] Stull and Prophet (1971).

[e] Griller and Lossing (1981).

[f] Demissy and Lesclaux (1980).

[g] Benson (1976).

[h] $\Delta H_f^0(NH\dot{N})$ obtained from $BDE(NH) = 59.8$ and $\Delta H_f^0(NHNH) = 50.7$ (Foner and Hudson, 1978).

[i] Foner and Hudson (1958).

[j] Fisher and Heath (1965).

[k] Benson and Nangia (1980).

Moreover, in the case of $\dot{N}H_2$, $\dot{N}O$, $CH_2\dot{N}$, $NH\dot{N}$, and $HO\dot{N}H$, we have used the particular isodesmic reaction:

$$R^{\cdot} + CH_3NH_2 \rightarrow RH + CH_3\dot{N}H$$

A quantitative relation between the semiempirical (SE) and experimental (E) heats of formation may be deduced from the results of Table XV. It is written as:

$$\Delta H_f^0(SE) = 0.1487 + 1.0261\Delta H_f^0(E) \qquad (r = 0.9974) \qquad (72)$$

TABLE XVI

PREDICTION OF SOME THERMOCHEMICAL DATA CONCERNING SMALL FREE RADICALS (IN KCAL MOL^{-1})

Radical	$\Delta H_f^0(298.15)$	BDE(R—H)[a]
$\dot{C}HNH$	76.95	102.65[b]
$CH_2\dot{N}$	54.80	80.50
$HO\dot{N}H$	29.03	90.13[c]
$NH_2\dot{O}$	16.16	77.26
$NH_2\dot{N}H$	52.96	82.26[c]

[a] Calculated from the predicted value of $\Delta H_f^0(R^\cdot)$ and the (estimated or experimental) value of $\Delta H_f^0(RH)$, with $\Delta H_f^0(H^\cdot) = 52.1$ (Cox and Pilcher, 1970).

[b] De Frees and Hehre (1978).

[c] Benson (1976).

This allows us to predict some thermochemical data not yet experimentally determined and to propose a unique value for the heat of formation of $NH_2\dot{N}H$ (see Table XVI).

B. Standard Entropies

The vibrational and rotational energy levels of small chemical species are easy to obtain, assuming the quadratic and rigid rotator approximations, respectively. If we further consider the system under consideration as an ideal gas, we may readily calculate its standard entropy using the classical formalism of statistical thermodynamics. This is particularly interesting in the case of transient free radicals, which are very difficult to study from the experimental point of view. The standard entropies of the previous series of small free radicals and parent molecules have been theoretically calculated using the above procedure. In Table XVII, we compare them with Benson's values (1976). For free radicals, these are deduced by group additivities from the properties of simple species, the latter being calculated from assumed structures and frequency assignments. The satisfactory agreement between theoretical and Benson's results is a justification of the empirical procedure of this author. However, our list of data is more coherent and complete. Combined with the data of Section III,A, they allow us to estimate the standard free enthalpy change of various types of free radical reactions.

TABLE XVII

STANDARD ENTROPIES OF SMALL CHEMICAL SPECIES[a]
(IN GIBBS MOL^{-1})

Radical	S^0	Molecule	S^0
$\dot{C}H_3$	46.4	CH_4	44.4
	(46.5)		(44.5)
$HC\equiv\dot{C}$	50.3	$HC\equiv CH$	47.2
	(49.6)		(48.3)
$H_2C{=}\dot{C}H$	55.8	$H_2C{=}CH_2$	52.4
	(56.3)		(52.4)
$\dot{C}N$	48.4	HCN	47.9
	(48.4)		(48.2)
$\dot{C}H_2NH_2$	61.6	CH_3NH_2	58.7
	(57.0)		(58.1)
$\dot{C}_2H_5$	58.1	C_2H_6	54.2
	(58.0)		(54.9)
$H\dot{C}{=}NH$	53.4	$H_2C{=}NH$	54.2
$\dot{N}H_2$	46.4	NH_3	46.2
	(46.5)		(46.0)
$H_2C{=}\dot{N}$	53.6	$HN{=}NH$	52.0
			(52.2)
$HN{=}\dot{N}$	53.6	NH_2OH	53.1
$HO\dot{N}H$	54.2	NH_2NH_2	55.6
			(57.1)
$NH_2\dot{N}H$	58.7	CH_3NH_2	58.7
			(58.1)
$CH_3\dot{N}H$	58.7	H_2O	44.9
	(57.0)		(45.1)
$\dot{O}H$	42.5	CH_3OH	57.0
	(43.9)		(57.3)
$CH_3\dot{O}$	56.4	NH_2OH	53.1
	(56.0)		
$NH_2\dot{O}$	59.0	$HOOH$	57.9
			(56.0)
$HO\dot{O}$	53.5	$H_2C{=}O$	53.2
	(54.4)		(52.3)
$H\dot{C}O$	53.3		
	(53.7)		
$\dot{C}H_2OH$	58.9		

[a] Benson's (1976) results in parentheses.

C. Stability: A Unifying Concept

1. *Introduction*

The concept of stability is widely used by chemists but, until quite recently, no general and unique definition of this notion had been proposed. Let us first point out that this concept may characterize either an "isolated" species without making reference to any actual chemical process or a given thermodynamical system generally containing various constituents capable of undergoing some chemical reaction. As one very well knows, that system is said to be *thermodynamically stable* if the corresponding standard chemical affinity is largely negative, which can be written:

$$A^0 \ll 0 \tag{73}$$

or, as

$$A^0 = -\Delta G^0 \tag{74}$$

$$\Delta G^0 \gg 0 \tag{75}$$

and, finally,

$$\Delta H^0 - T\Delta S^0 \gg 0 \tag{76}$$

When this condition is fulfilled, the system is thermodynamically inert, i.e., the reaction under consideration is "impossible."

If we adopt a kinetic point of view, we shall define the stability of a compound by its lifetime under given experimental conditions. We can also use the rate constant or, restrictively, the activation energy of a chosen reaction of the corresponding thermodynamical system. This type of stability is related to the concept of *kinetic stabilization,* which has been carefully analyzed by Griller and Ingold (1976) in the case of free radicals. These authors introduce various adjectives to characterize the kinetic stabilization of these species. A given radical is said to be *transient* if its lifetime is comparable to that of a methyl radical under the same experimental conditions. In solution, the rate constant for the process by which the transient radical decays approaches the diffusion-controlled limit. A *persistent* radical has a lifetime significantly greater than methyl under the same experimental conditions. Finally, a pure radical is *kinetically stable* if it can be handled and stored without special precautions. It is obvious that a thermodynamically stable system will also be kinetically stable (of course if one refers to the same reaction), but the reverse is not necessarily true.

For defining an intrinsic stability of a chemical species we start from the common assumption (Cox and Pilcher, 1970) that the heat of atomization of a molecule (generally taken at 298.15 K) is equal to its total chemical binding energy. This quantity may be written as a sum of three terms corresponding, respectively, to the bond energies and to stabilizing and destabilizing contributions:

$$\Delta H_a^0 = \begin{cases} \Sigma \text{ chemical bond energies } + \\ \Sigma \text{ destabilization energies } + \\ \Sigma \text{ stabilization energies} \end{cases} \tag{77}$$

Now we assume that the heat of atomization of some species, which we will refer to as *reference compounds,* is simply a sum of chemical bond energies or bond energy terms supposed to be constant and transferable from one species to another. Thus, for these reference compounds, Eq. (77) becomes:

$$\Delta H_a^0 = \Sigma\, N_{AB} E_{AB} \tag{78}$$

It allows us to determine a wide variety of bond energy terms from the experimental heats of atomization of reference compounds.

Then, these bond energy terms may be used to estimate the sum of stabilization and destabilization energies of any chemical species. These two contributions being hardly separable when they appear simultaneously in a given compound, we have defined (Leroy, 1983a) a conventional *stabilization energy, SE^0*, either positive or negative, as the difference between the heat of atomization and the sum of bond energy terms of the species under consideration. Thus, we will use the fundamental equation:

$$SE^0 = \Delta H_a^0 - \Sigma\, N_{AB} E_{AB} \tag{79}$$

where ΔH_a^0 is the heat of atomization either experimentally or semiempirically determined. Equation (79) provides the simplest definition of the *thermodynamical stabilization* of a chemical species. This definition is quite general, for it applies to any molecule, free radical, and positive and negative ion. Moreover, the concept of stabilization energy achieves a synthesis of various former notions which at first sight could seem unrelated, such as hyperconjugation, resonance, ring strain, and steric repulsion energies. Finally, it does not explicitly refer to any chemical reaction and can then be considered as an intrinsic property of the species under consideration.

Before we analyze the results obtained for a large variety of compounds, we recall the main formulas we have previously deduced for calculating the stabilization energy of neutral species, molecules and free radicals, and of ionic species, carbocations and carbanions. Furthermore, we shall briefly describe our bond energy scheme and provide a detailed list of recommended values of bond energy terms.

2. *Computational Details*

a. Stabilization energy expressions. The stabilization energy of a neutral species is defined by Eq. (79). The atomization process corresponds to the reaction:

$$\text{molecule (radical)(g)} \rightarrow \text{atoms(g)}$$

all the species being in their ground state. Thus we may write:

$$\Delta H_a^0 = \Delta H_f^0(\text{atoms}) - \Delta H_f^0(\text{molecule or radical}) \tag{80}$$

The heats of formation of some gaseous atoms from the elements in their reference state are given in Table XVIII.

The stabilization energies of carbocations and carbanions are, respectively, written as:

$$SE^0(\mathrm{R}^+) = SE^0(\mathrm{R}^{\cdot}) - I(\mathrm{R}^{\cdot}) + I(\mathrm{C}) \tag{81}$$

and

$$SE^0(\mathrm{R}^-) = SE^0(\mathrm{R}^{\cdot}) + A(\mathrm{R}^{\cdot}) - A(\mathrm{C}) \tag{82}$$

where $SE^0(\mathrm{R}^{\cdot})$ is the stabilization energy of the corresponding radical; I, the ionization potential; and A, the electron affinity of the species given in parentheses [$I(\mathrm{C})$ = 259.65 kcal mol^{-1} (Rosenstock *et al.*, 1977) and $A(\mathrm{C})$ = 29.33 kcal mol^{-1} (Hotop and Lineberger, 1975)].

TABLE XVIII

HEATS OF FORMATION OF GASEOUS ATOMS IN THEIR GROUND STATE AT 298.15 K (IN KCAL G ATOM^{-1})[a]

Atom	$\Delta H_f^0(\mathrm{g})$
H	52.10
C	170.90
N	113.00
O	59.56
F	18.86
S	65.65
Cl	28.92
Br	26.74
I	25.54

[a] Cox and Pilcher (1970).

b. Description of the bond energy scheme. A detailed description of our bond energy scheme has been given elsewhere (Leroy, 1983a). Thus, we shall only recall here some typical features of our procedure. The chosen series of reference compounds, respectively, are

1. Linear and little-branched alkanes: RH.
2. Monosubstituted alkanes: RX with X = halogen atom or functional group (OH, OR, OOR, SH, SR, SSR, NH_2, NHR, NNH_2, NNHR, CHO, COR, COOH, CN, NO_2).
3. Monoolefines.
4. Alkynes.

The general expression of the heat of atomization is written as:

$$\begin{aligned}\Delta H_a = {} & N_{CC}E(\text{C—C}) + N_pE(\text{C—H})_p + N_sE(\text{C—H})_s + N_tE(\text{C—H})_t \\ & + N_{CX}E(\text{C—X}) + N_p^x(\text{C—H})_p^x + N_s^xE(\text{C—H})_s^x + N_t^xE(\text{C—H})_t^x \\ & + N_{XH}E(\text{X—H}) \qquad (83)\end{aligned}$$

for series (1) and (2), and

$$\begin{aligned}\Delta H_a = {} & N_{CC}E(\text{C—C}) + N_pE(\text{C—H})_p + N_sE(\text{C—H})_s + N_tE(\text{C—H})_t \\ & + N_{C_dC}E(\text{C}_d\text{—C}) + N_1E(\text{C}_d\text{—H})_1 + N_2E(\text{C}_d\text{—H})_2 \\ & + N_{C_xC}E(\text{C}_x\text{—C}) + E(\text{C=C}) \qquad (84)\end{aligned}$$

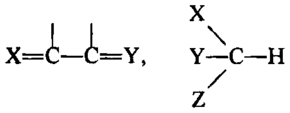
or

$$\begin{aligned}\Delta H_a = {} & N_{CC}E(\text{C—C}) + N_pE(\text{C—H})_p + N_sE(\text{C—H})_s + N_tE(\text{C—H})_t \\ & + N_{C_tC}E(\text{C}_t\text{—C}) + N_{C_tH}E(\text{C}_t\text{—H}) \\ & + E(\text{C}\equiv\text{C}) \qquad (85)\end{aligned}$$

for the monoolefine and alkyne series, respectively.

If the above procedure is adopted, all the reference compounds have a nonsignificant (if any) stabilization energy. However, as the choice of reference compounds is quite arbitrary, we may systematically use the bond energy terms of the alkane series and so calculate nonnegligible stabilization energies for the species of the other series. In fact, the choice of the reference compounds and therefore the bond parameters to be used depends only on the effect we want to analyze. Some illustrations of this remark are given below.

c. Recommended values of bond parameters. The bond energy terms listed in Table XIX have been determined by the least-square method using the MULFRA computer program (Sana, 1981c). Moreover, some specific increments have been introduced. Indeed, for compounds such as



the problem arises as to what value should be ascribed either to the C—C or to the C—H bond energy term. In order to take account independently of the influence of each substituent on the bond under consideration, we have defined specific increments by the following relations:

$$E(\mathrm{C}_x\text{—C}) = E(\text{C—C}) + \Delta(\mathrm{C}_x\text{—C}) \qquad (86)$$

TABLE XIX

RECOMMENDED VALUES OF BOND ENERGY TERMS (IN KCAL)[a]

$E(\text{C—C})$	85.05	$E(\text{C—N})$	76.61	$E(\text{C—F})$	109.50
$E(\text{C—H})_p$	98.25	$E(\text{N—H})_2$	91.31	$E(\text{C—H})_p^{\text{F}}$	97.79
$E(\text{C—H})_s$	97.50	$E(\text{N—H})_1$	90.29	$E(\text{C—H})_s^{\text{F}}$	97.26
$E(\text{C—H})_t$	96.78	$E(\text{C—H})_p^{\text{N}}$	96.75	$E(\text{C—H})_t^{\text{F}}$	96.56
$E(\text{C=C})$	136.77	$E(\text{C—H})_s^{\text{N}}$	96.27	$E(\text{N—F})$	64.70
$E(\text{C}_d\text{—C})$	88.92	$E(\text{C—H})_t^{\text{N}}$	95.87		
$E(\text{C}_d\text{—H})_2$	100.24	$E(\text{N—N})$	47.88	$E(\text{C—Cl})$	85.56
$E(\text{C}_d\text{—H})_1$	99.72	$E(\text{S—S})$	61.99	$E(\text{C—H})_p^{\text{Cl}}$	96.72
$E(\text{C}\equiv\text{C})$	184.50	$E(\text{C—H})_p^{\text{SS}}$	97.71	$E(\text{C—H})_s^{\text{Cl}}$	96.38
$E(\text{C}_t\text{—C})$	93.93	$E(\text{C—H})_s^{\text{SS}}$	97.27	$E(\text{C—H})_t^{\text{Cl}}$	95.83
$E(\text{C}_t\text{—H})$	103.51				
		$E(\text{C—NO}_2)$	290.53	$E(\text{C—Br})$	71.50
$E(\text{C—O})$	91.33	$E(\text{NO}_2)$	213.92	$E(\text{C—H})_p^{\text{Br}}$	97.11
$E(\text{O—H})$	108.12	$E(\text{C—H})_p^{\text{NO}_2}$	95.56	$E(\text{C—H})_s^{\text{Br}}$	96.71
$E(\text{C—H})_p^{\text{O}}$	95.86	$E(\text{C—H})_s^{\text{NO}_2}$	94.32	$E(\text{C—H})_t^{\text{Br}}$	96.78
$E(\text{C—H})_s^{\text{O}}$	95.49	$E(\text{C—H})_t^{\text{NO}_2}$	92.62		
$E(\text{C—H})_t^{\text{O}}$	95.35	$E(\text{N=O})$	119.35	$E(\text{C—I})$	55.87
$E(\text{O—O})$	46.14	$E(\text{N—O})$	47.12	$E(\text{C—H})_p^{\text{I}}$	97.73
$E(\text{C—H})_p^{\text{OO}}$	95.79			$E(\text{C—H})_s^{\text{I}}$	97.51
$E(\text{C—H})_s^{\text{OO}}$	95.35	$E(\text{C—CN})$	297.62	$E(\text{C—H})_t^{\text{I}}$	97.42
$E(\text{C=O})$	160.17	$E(\text{C}\equiv\text{N})$	203.69		
$E(\text{C}_{\text{CO}}\text{—H})_2$	100.24	$E(\text{C—H})_p^{\text{CN}}$	99.37		
$E(\text{C}_{\text{CO}}\text{—H})_1$	101.33	$E(\text{C—H})_s^{\text{CN}}$	98.14		
$E(\text{C}_{\text{CO}}\text{—C})$	93.68	$E(\text{C—H})_t^{\text{CN}}$	98.23		
$E(\text{C—H})_p^{\text{CO}}$	98.25				
$E(\text{C—H})_s^{\text{CO}}$	97.41	$E(\text{C—S})$	71.63		
$E(\text{C—H})_t^{\text{CO}}$	96.33	$E(\text{S—H})$	85.30		
$E(\text{COOH})$	383.96	$E(\text{C—H})_p^{\text{S}}$	97.67		
		$E(\text{C—H})_s^{\text{S}}$	97.35		
		$E(\text{C—H})_t^{\text{S}}$	96.75		

[a] Least-square results: residual sum of square deviates, 7.6726; mean deviate, 0.0000; residual variance, 0.3957; highest deviate, −0.9743; multiple correlation coefficient, 0.9999.

$$E(\mathrm{C{-}H})_i^x = E(\mathrm{C{-}H})_i + \Delta(\mathrm{C{-}X})_i^x \qquad (87)$$

where subscript *i* refers to the nature of the C—H bond (primary, secondary, or tertiary).

Thus, for example, the bond energy term of the central C—C bond of butadiene is written as:

$$E(\mathrm{C_d{-}C_d}) = E(\mathrm{C{-}C}) + 2\Delta(\mathrm{C_d{-}C}) \qquad (88)$$

The recommended values of bond increments are collected in Table XX.

3. *Applications of the Concept of Stabilization Energy*

a. Substituted methanes. Most of the substituted methanes listed in Table XXI exhibit a large negative SE^0 which is probably due either to both steric and electronic factors (tri- and tetrasubstituted derivatives) or

TABLE XX

RECOMMENDED VALUES OF BOND INCREMENTS (IN KCAL)

$\Delta(\mathrm{C_{CO}{-}C})$	8.63	$\Delta(\mathrm{C{-}H})_p^{Cl}$	−1.53
$\Delta(\mathrm{C_d{-}C})$	3.87	$\Delta(\mathrm{C{-}H})_s^{Cl}$	−1.12
$\Delta(\mathrm{C_t{-}C})$	8.88	$\Delta(\mathrm{C{-}H})_t^{Cl}$	−0.95
$\Delta(\mathrm{C_{CN}{-}C})$	8.88		
		$\Delta(\mathrm{C{-}H})_p^{Br}$	−1.14
$\Delta(\mathrm{C{-}H})_p^{O}$	−2.39	$\Delta(\mathrm{C{-}H})_s^{Br}$	−0.79
$\Delta(\mathrm{C{-}H})_s^{O}$	−2.01	$\Delta(\mathrm{C{-}H})_t^{Br}$	0.00
$\Delta(\mathrm{C{-}H})_t^{O}$	−1.43		
		$\Delta(\mathrm{C{-}H})_p^{I}$	−0.52
$\Delta(\mathrm{C{-}H})_p^{N}$	−1.50	$\Delta(\mathrm{C{-}H})_s^{I}$	0.01
$\Delta(\mathrm{C{-}H})_s^{N}$	−1.23	$\Delta(\mathrm{C{-}H})_t^{I}$	0.64
$\Delta(\mathrm{C{-}H})_t^{N}$	−0.91		
		$\Delta(\mathrm{C{-}H})_p^{CO}$	0.00
$\Delta(\mathrm{C{-}H})_p^{OO}$	−2.46	$\Delta(\mathrm{C{-}H})_s^{CO}$	−0.09
$\Delta(\mathrm{C{-}H})_s^{OO}$	−2.15	$\Delta(\mathrm{C{-}H})_t^{CO}$	−0.45
$\Delta(\mathrm{C{-}H})_p^{CN}$	1.12	$\Delta(\mathrm{C{-}H})_p^{S}$	−0.58
$\Delta(\mathrm{C{-}H})_s^{CN}$	0.64	$\Delta(\mathrm{C{-}H})_s^{S}$	−0.15
$\Delta(\mathrm{C{-}H})_t^{CN}$	1.45	$\Delta(\mathrm{C{-}H})_t^{S}$	−0.03
$\Delta(\mathrm{C{-}H})_p^{NO_2}$	−2.69	$\Delta(\mathrm{C{-}H})_p^{SS}$	−0.54
$\Delta(\mathrm{C{-}H})_s^{NO_2}$	−3.18	$\Delta(\mathrm{C{-}H})_s^{SS}$	−0.23
$\Delta(\mathrm{C{-}H})_t^{NO_2}$	−4.16		
$\Delta(\mathrm{C{-}H})_s^{F}$	−0.24		
$\Delta(\mathrm{C{-}H})_t^{F}$	−0.22		

TABLE XXI

STABILIZATION ENERGIES OF SOME SUBSTITUTED METHANES (IN KCAL MOL^{-1})

Compound	ΔH_a^0 Calc.	ΔH_a^0 Exp.[a]	SE^0
$C(NO_2)_4$	1162.12	1080.18[b]	−81.94
$CCl(NO_2)_3$	957.15	981.85	−65.30
$CH(NO_2)_3$	955.89	919.53	−36.36
CCl_3Br	328.18	294.61	−33.57
CCl_4	342.24	309.81	−32.43
$CHCl_3$	350.61	334.81	−15.80
$CH_2(CN)_2$	792.80	779.44	−13.36
$CH_2(NO_2)_2$	763.34	753.42	−9.92
$CH_2(CN)(OH)$	689.33	682.14[c]	−7.19
CH_2Cl_2	361.64	355.81	−5.83
$CH_2(CN)(NH_2)$	750.67	748.26[c]	−2.41
$CH_2(NH_2)(COOH)$	929.23	928.56	−0.67
$CH_2(OCH_3)_2$	1127.44	1131.84	4.40
$CH_2(OH)_2$	585.86	591.42	5.56
CH_2F_2	413.04	420.82[d]	7.78
CHF_3	425.06	440.28[d]	15.22

[a] All the data except those corresponding to the following references are taken from Pedley and Rylance (1977).

[b] Cox and Pilcher (1970).

[c] Semiempirical values (Leroy and Peeters, 1981).

[d] Benson (1976).

to electronic effects of substituents only. The latter could be interpreted in terms of electrostatic interaction between polar groups.

However, as stated by various authors (Cox and Pilcher, 1970), this type of interaction can have a stabilizing effect that could explain the positive SE^0 of fluoro and oxygen derivatives.

b. Steric repulsion in highly branched alkanes. The SE^0 values collected in Table XXII clearly demonstrate that important steric repulsion occurs in highly branched alkanes. This was already pointed out by Cox and Pilcher (1970), who used a four-parameter scheme for the estimation of the total strain energy of such compounds. Our results are similar to those obtained by these authors.

c. Substituted ethanes. The SE^0 values of a large variety of substituted ethanes have been calculated using either semiempirical heats of formation (Leroy *et al.*, 1983b) or experimental data if they were available. The results obtained are listed in Table XXIII according to the type of substituents.

TABLE XXII

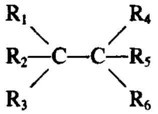
Stabilization Energies of Some Highly Branched Alkanes (in kcal mol^{-1})

Alkane skeleton	ΔH_a^0 Calc.	ΔH_a^0 Exp.[a]	SE^0
CCC CCCCC CC	2925.48	2912.87	−12.61
CCC CCCCC C C	2925.48	2914.41	−11.07
CCC CCCCC C C	2922.51	2913.41	−9.10
C C CCCCC CC C	2921.07	2912.29	−8.78
CC CCCCC CC	2643.90	2636.77	−7.13
C C CCCCCC C C	2919.45	2915.49	−3.96
C C CCCCC C C	2639.40	2635.75	−3.65
CC CCCCCC C	2640.93	2637.80	−3.13

[a] Somayajulu *et al.* (1977).

TABLE XXIII

STABILIZATION ENERGIES OF VARIOUS SUBSTITUTED ETHANES (IN KCAL MOL^{-1})



R_1	R_2	R_3	R_4	R_5	R_6	ΔH_f^0	SE^0
F	H	H	F	H	H	−103.88[a]	−1.29
F	H	H	F	F	H	−159.44[a]	9.71
H	H	H	F	F	H	−119.70[b]	12.48
F	F	H	F	F	H	−213.84[a]	19.55
F	H	H	F	F	F	−216.59[a]	20.46
F	F	H	F	F	F	−264.00[b]	23.31
H	H	H	F	F	F	−178.20[b]	24.58
F	F	F	F	F	F	−320.90[b]	33.81
OH	H	H	OH	H	H	−92.70[c]	0.31
OH	H	H	OH	OH	H	−136.67[a]	1.45
H	H	H	OH	OH	H	−102.71[a]	3.62
OH	OH	H	OH	OH	H	−181.82[a]	3.77
OH	H	H	OH	OH	OH	−186.58[a]	5.39
OH	OH	H	OH	OH	OH	−229.94[a]	5.92
H	H	H	OH	OH	OH	−152.27[a]	7.20
OH	OH	OH	OH	OH	OH	−277.92[a]	7.93
CH_3	CH_3	H	CH_3	CH_3	H	−42.61[d]	−0.40
CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	−53.83[d]	−5.02
$C(CH_3)_3$	$C(CH_3)_3$	H	CH_3	CH_3	CH_3	−53.69[e]	−35.94
$C(CH_3)_3$	$C(CH_3)_3$	H	$C(CH_3)_3$	$C(CH_3)_3$	H	−71.35[f]	−49.06
C_6H_5	H	H	C_6H_5	H	H	32.40[d]	−0.23
C_6H_5	CH_3	H	C_6H_5	CH_3	H	23.18[g]	−3.97
C_6H_5	$CH(CH_3)_2$	H	C_6H_5	$CH(CH_3)_2$	H	4.10[g]	−7.75
C_6H_5	CH_3	CH_3	C_6H_5	CH_3	CH_3	14.30[h]	−10.93
C_6H_5	$C(CH_3)_3$	H	C_6H_5	$C(CH_3)_3$	H	−2.70[h]	−16.79
C_6H_{11}	CH_3	CH_3	C_6H_{11}	CH_3	CH_3	−71.90[i]	−19.01
C_6H_{11}	C_2H_5	CH_3	C_6H_{11}	C_2H_5	CH_3	−71.60[j]	−29.21
C_6H_{11}	$C(CH_3)_3$	H	C_6H_{11}	$C(CH_3)_3$	H	−79.40[f]	−34.37
CN	H	H	CN	H	H	50.12[k]	−4.97
H	H	H	CN	CN	H	58.12[a]	−14.84
CN	H	H	CN	CN	H	93.95[a]	−18.02
H	H	H	CN	CN	CN	104.4[l]	−26.66
CN	CN	H	CN	CN	H	139.78[a]	−33.07
CN	H	H	CN	CN	CN	149.06[a]	−39.27
CN	CN	H	CN	CN	CN	193.36[a]	−52.79
CN	CN	CN	CN	CN	CN	247.80[a]	−73.37

TABLE XXIII (*Continued*)

R_1	R_2	R_3	R_4	R_5	R_6	ΔH_f^0	SE^0
Cl	H	H	Cl	H	H	−30.7[d]	−2.95
H	H	H	Cl	Cl	H	−31.1[m]	−6.66
Cl	H	H	Cl	Cl	H	−35.5[d]	−9.00
H	H	H	Cl	Cl	Cl	−34.01[m]	−17.61
Cl	Cl	H	Cl	Cl	H	−35.9[d]	−19.47
Cl	H	H	Cl	Cl	Cl	−35.7[m]	−22.67
Cl	Cl	H	Cl	Cl	Cl	−34.8[m]	−34.43
Cl	Cl	Cl	Cl	Cl	Cl	−33.2[m]	−49.89
CN	CH_3	CH_3	CN	CH_3	CH_3	24.16[n]	−5.25
CN	OH	H	CN	OH	H	−22.30[a]	−13.30
CN	CH_3 CH_2CH CH_3	CH_3 CH_2CH CH_3	CN	CH_3 CH_2CH CH_3	CH_3 CH_2CH CH_3	−26.70[o]	−19.92
C_6H_5	CN	OCH_3	C_6H_5	CN	OCH_3	40.60[p]	−21.23

[a] Semiempirical values obtained by using appropriate isodesmic reactions (Leroy *et al.*, 1983b).

[b] Chen *et al.* (1975).

[c] Gardner and Hussain (1972).

[d] Cox and Pilcher (1970).

[e] Rüchardt and Weiner (1979).

[f] Beckhaus *et al.* (1978a,b).

[g] Hellmann *et al.* (1979).

[h] Beckhaus (1983).

[i] Winiker *et al.* (1980).

[j] Beckhaus *et al.* (1980).

[k] Rapport *et al.* (1971).

[l] Chu *et al.* (1982).

[m] Chao *et al.* (1974).

[n] Pedley and Rylance (1977).

[o] Barbe *et al.* (1983).

[p] Rüchardt and Beckhaus (1983).

It is seen that hydroxy derivatives and, to a larger extent, fluoro derivatives are stabilized, all the other substituted ethanes considered here being more or less destabilized depending on the nature, the number, and the position of the substituents. Electrostatic interaction between polar groups might be invoked for explaining both the stabilizing effect of fluorine and hydroxyl substituents and the destabilizing effect of cyano groups. However, an explicit calculation of this type of interaction is hardly feasible. Both steric and electronic factors are presumably to be considered in highly destabilized chloroethanes and the last two compounds of Table XXIII. Finally, steric factors alone are very likely responsible for the large destabilization of aryl-, alkyl-, and cyclohexyl-substituted ethanes.

We will show later on that the results of Table XXIII may be used for rationalizing thermochemical data such as C—C and C—H bond dissociation energies and also the reactivity of carbon-centered radicals.

d. Nonaromatic cyclic compounds. The (negative) stabilization energy of an unsubstituted cyclic compound is nothing else (the sign apart) but its conventional ring-strain energy (CRSE). On the other hand, the stabilization energy of a substituted cyclic species may contain additional contributions such as a steric repulsion energy and those corresponding to

TABLE XXIV

STABILIZATION ENERGIES OF SOME CYCLOALKANES AND CYCLOALKENES (IN KCAL MOL^{-1})

Compound	ΔH_a^0 Calc.	ΔH_a^0 Exp.[a]	SE^0
Cyclopropane	840.15	812.56	−27.59
Cyclobutane	1120.20	1093.30	−26.90
Cyclopentane	1400.25	1394.24	−6.01
Cyclohexane	1680.30	1680.07	−0.23
Cyclopropene	709.50	654.87	−54.18
Cyclobutene	989.10	958.75	−30.35
Cyclopentene	1269.15	1263.48	−5.67
Cyclohexene	1549.20	1547.50	−1.70
Cyclopentadiene	1138.05	1135.84	−2.21
p-Quinodimethane	1718.08	1727.90[b]	9.82
Cyclopentanol	1500.05	1493.03	−7.02
Methylcyclopentane	1681.83	1675.91	−5.92
Cyclohexanone	1662.37	1659.90	−2.47
Cyclohexanol	1780.10	1778.71	−1.39
Cyanocyclohexane	1881.15	1861.61	0.46
Methylcyclohexane	1961.88	1962.68	0.80
1,1-Dimethylcyclohexane	2244.90	2244.03	−0.87
cis-1,2-Dimethylcyclohexane	2243.46	2241.93	−1.53
trans-1,2-Dimethylcyclohexane	2243.46	2243.79	0.33
cis-1,3-Dimethylcyclohexane	2243.46	2244.93	1.47
trans-1,3-Dimethylcyclohexane	2243.46	2242.98	−0.48
cis-1,4-Dimethylcyclohexane	2243.46	2243.00	−0.46
trans-1,4-Dimethylcyclohexane	2243.46	2244.90	1.44

[a] All the data are taken from Cox and Pilcher (1970) except that for *p*-quinodimethane.

[b] Dewar (1982).

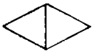
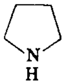
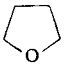
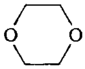
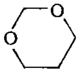
electronic effects of substituents. We have calculated the SE^0 values for a series of saturated and unsaturated cyclic molecules eventually substituted (Table XXIV), a few multiring alkanes, and some saturated heterocyclic compounds (Table XXV).

Our results are very similar to the corresponding data of the literature and they can be interpreted in the same way (Cox and Pilcher, 1970, and references therein). However, in the case of cis and trans dimethylcyclohexanes, there are some discrepancies between our SE^0 values and the steric repulsion energies calculated by Skinner. Still, the two series of results give the same order of stability as the heats of atomization, which obviously remain the best criterion for comparing the stabilities of isomers.

e. Alkyl-substituted alkenes. The SE^0 values of alkyl-substituted alkenes do not reveal hyperconjugation effects because propene is a reference compound in our bond energy scheme. However, using a six-parameter scheme in which $E(C_d—C) = E(C—C)$ and $E(C_d—H)_1 = E(C_d—H)_2$, we may define a global stabilization energy (GSE^0) that reveals all the effects which are present in the compound under consideration, i.e., es-

TABLE XXV

STABILIZATION ENERGIES FOR SOME MULTIRING ALKANES AND SATURATED HETEROCYCLIC COMPOUNDS (IN KCAL MOL^{-1})

Compounds	ΔH_a^0 Calc.	ΔH_a^0 Exp.[a]	SE^0
	1008.81	944.30	−64.51
	1290.30	1227.05	−63.25
	1273.74	1266.31	−7.43
	1209.77	1203.98	−5.79
	1299.34	1295.05	−4.29
	1299.34	1303.17	3.83

[a] Cox and Pilcher (1970).

sentially, stabilizing hyperconjugation, interaction between alkyl groups through the double bond, and destabilizing steric repulsion. Only the latter two should be revealed by our usual stabilization energy (SE^0).

The SE^0 and GSE^0 values of a series of alkyl-substituted alkenes are collected in Table XXVI. It is seen that the (stabilizing) hyperconjugation energy is approximately equal to 3.2 kcal mol^{-1}, whatever the alkyl group attached to the double bond may be. Moreover, the global stabilization of *cis*-2-butene is smaller than that of *trans*-2-butene due to the steric repulsion between the methyl groups in cis position.

The heat of hydrogenation of the chosen alkenes is also given in Table XXVI. This quantity is commonly used for defining the resonance energy (RE^0) of any unsaturated compound. In fact, that RE^0 is nothing else but the heat of reaction of the following process:

$$\begin{matrix}\text{unsaturated} \\ \text{compound}\end{matrix} + \begin{matrix}\text{reference} \\ \text{alkane}\end{matrix} \rightarrow \begin{matrix}\text{saturated} \\ \text{compound}\end{matrix} + \begin{matrix}\text{reference} \\ \text{alkene}\end{matrix}$$

Its value obviously depends on the choice of the reference alkene. The results obtained using ethylene as reference compound are also listed in Table XXVI. It is seen that they do not always provide the correct order of stability. Indeed, according to RE^0 values, 2-methylpropene should be less stable than *trans*-2-butene, and 3-methyl-*trans*-2-pentene, more stable than 2,3-dimethyl-2-butene, which is in contradiction with the information directly given by the corresponding heats of atomization.

It is worth noticing that the so-defined resonance energy shall be equal to our global stabilization energy if and only if the sum of the bond energy

TABLE XXVI

THERMODYNAMICAL PROPERTIES OF ALKYL-SUBSTITUTED ALKENES (IN KCAL MOL^{-1})

Compound	ΔH_a^0[a]	ΔH^0 (Hyd.)[a]	RE^0	GSE^0	SE^0
Propene	820.77	−29.81	2.75	3.18	−0.17
1-Butene	1100.50	−30.33	2.23	3.16	−0.19
cis-2-Butene	1102.26	−28.37	4.19	5.41	−1.29
trans-2-Butene	1103.39	−27.24	5.32	6.54	−0.16
2-Methylpropene	1104.44	−28.11	4.45	7.74	0.15
1-Pentene	1380.73	−29.78	2.78	3.34	1.03
trans-2-Pentene	1383.32	−27.19	5.37	6.42	−0.20
2-Methyl-2-butene	1385.56	−26.70	5.86	9.15	−1.94
1-Hexene	1660.54	−30.00	2.56	3.10	0.79
trans-3-Hexene	1663.60	−26.94	5.62	6.65	−0.05
3-Methyl-*trans*-2-pentene	1665.68	−26.05	6.51	9.22	−1.87
2,3-Dimethyl-2-butene	1667.16	−26.32	6.24	11.19	−4.29

[a] Pedley and Rylance (1977).

terms of the reagents of the above-mentioned reaction process is equal to that of the products and, particularly, if the reference molecules and the saturated compound are not stabilized or destabilized. These two requirements never strictly meet, whatever bond energy scheme may be assumed. Thus, we strongly advise against the use of resonance energies derived from heats of atomization.

In fact, this remark is absolutely general and can be stated as: a heat of reaction may never be used for determining any property of one of the compounds involved in that reaction. Various illustrations of this remark will be given later on.

f. Other substituted alkenes. The stabilization energies of ethylenes substituted by heteroatoms or functional groups represent not only both π-delocalization energy and electrostatic interaction energy between polar groups but also the steric repulsion energy between bulky substituents, if any. In general, as shown in Table XXVII, these effects are altogether destabilizing. It is also seen that the SE^0 values of polychloroethylenes are quite similar to those of the corresponding saturated compounds (see Table XXIII).

Here again, we can define a global stabilization energy for each species with respect to ethylene. These quantities, which contain the contributions of all possible effects, are also listed in Table XXVII. One will

TABLE XXVII

THERMODYNAMICAL PROPERTIES OF ETHYLENES SUBSTITUTED BY HETEROATOMS OR FUNCTIONAL GROUPS (IN KCAL MOL^{-1})

Compound	ΔH_a^0[a]	ΔH^0 (Hyd.)[a]	RE^0	SE^0	GSE^0
CH_2=CH—Cl	518.11	−35.70	−3.14	−3.47	−4.94
CH_2=CH—Br	505.89	−33.84	−1.28	−2.58	−3.10
CH_2=CH—CN	738.81	−30.88	1.68	−1.10	3.70
CH_2=CH—O—CH_2—CH_3	1193.63	−26.49	6.07	4.65	4.96
CN—CH=CH—CN (cis)	932.50	−31.18	1.38	−9.59	0.00
CH_2=CF_2	564.82[b]	−38.30[b]	−5.74	8.57	8.57
F—CH=CF_2	567.78[b]	−42.14[c]	−9.58	2.96	3.48
CH_2=CCl_2	503.29	−31.20	1.36	−5.08	−5.08
Cl—CH=CH—Cl (trans)	502.64	−32.20	0.36	−2.79	−5.73
Cl—CH=CH—Cl (cis)	502.76	−32.08	0.48	−2.67	−5.61
CN—CH=C$(CN)_2$	1121.20	—	—	−21.21	−8.67
Cl—CH=CCl_2	482.64	−33.52	−0.96	−9.58	−11.05
$(CN)_2$C=C$(CN)_2$	1308.76	—	—	−33.97	−18.49
Cl_2C=CCl_2	459.61	−33.65	−1.09	−19.40	−19.40

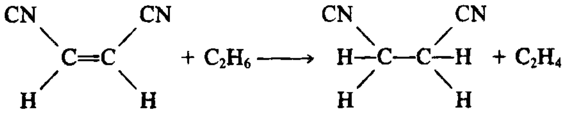
[a] Pedley and Rylance (1977).

[b] Cox and Pilcher (1970).

[c] $\Delta H_f^0(CH_2F{-}CHF_2)$: see Table XXIII.

note that very few species have a positive GSE^0. Furthermore, the heat of hydrogenation and the related RE^0 of the various compounds do not provide any information on their thermodynamic stabilization (see Table XXVII). This is due to the relatively large stabilization energy of the corresponding alkane and, in some cases, to the nonisodesmic character of the reaction which is considered for defining the resonance energy.

For example, the empirical RE^0 of dicyano-*cis*-ethylene is the heat of reaction of the fictitious process (reduction by ethane):



It may be written:

$$\Delta H^0 = -\sum_i k_iN_i(\Delta H_a)_i = -\sum_i k_iN_i\left(\sum E_{AB}\right)_i - \sum_i k_iN_i(SE^0)_i \qquad (89)$$

Using the data of Tables XIX, XXIII, and XXVII, one readily obtains (in kcal mol^{-1})

$$\Delta H^0 = 6.00 + SE^0(\text{alkene}) - SE^0(\text{alkane}) \qquad (90)$$

$$\Delta H^0 = 6.00 - \underline{9.59} - (-4.97) = \underline{1.38} = RE^0 \qquad (91)$$

It is clearly seen that the empirical resonance energy is a composite quantity which may be very different from the stabilization energy of the species under consideration.

g. Conjugated olefines. Depending on the choice of the bond energy terms, we may calculate either the stabilization energy (SE^0) or the global stabilization energy (GSE^0) of conjugated olefines. For open-chain species, the former essentially reveals conjugative and, if any, steric effects. On the other hand, for cyclic compounds, SE^0 may also contain a contribution due to ring strain. The global stabilization energy of conjugated olefines can be attributed to all possible stabilizing and destabilizing effects which are present in the species under consideration. Some examples are given in Table XXVIII. As expected, SE^0 as well as GSE^0 increases with the number of conjugated double bonds. Once again, we must point out that our SE^0 values are generally not equal to the resonance energies derived from heats of hydrogenation.

h. Miscellaneous compounds containing benzene ring(s). The stabilization energy of benzene results only from the delocalization of π electrons. It differs from the empirical resonance energy (RE^0) mainly owing to the stabilization energy of the reference alkene commonly chosen, i.e., cyclohexene. The SE^0 values of some condensed-ring hydrocarbons are

TABLE XXVIII

Stabilization and Global Stabilization Energies of Some Conjugated Olefines (in kcal mol^{-1})

Compound	ΔH^0_a	SE^0	GSE^0
2,3-Dimethyl-1,3-butadiene	1535.91[a]	1.28	16.76
2-Methyl-1,3-butadiene	1253.30[a]	2.62	13.71
cis-1,3-Butadiene	967.43[b]	0.70	7.40
trans-1,3-Butadiene	969.93[a]	3.20	9.90
cis-1,3-Pentadiene	1251.92[a]	2.28	12.33
trans-1,3-Pentadiene	1253.18[a]	3.54	13.59
cis-1,3,5-Hexatriene	1401.64[c]	5.91	19.31
trans-1,3,5-Hexatriene	1402.74[c]	7.01	20.41

[a] Pedley and Rylance (1977).
[b] Carreira (1975).
[c] Doering and Beasley (1973).

listed in Table XXIX. As their values are not directly comparable, we define a stabilization energy per π electron which shows that all these compounds have comparable SE^0 values, although some of them do not satisfy the $4n + 2$ Hückel rule.

Table XXX collects the SE^0 values of some conjugated hydrocarbons containing at least one benzene ring. These are attributable to π-electron

TABLE XXIX

Stabilization Energies of Condensed-Ring Hydrocarbons (in kcal mol^{-1})

Compound	ΔH^0_a[a]	SE^0	SE^0/N_π
Benzene (C_6H_6)	1318.19	31.19	5.20
Naphthalene ($C_{10}H_8$)	2089.85	51.50	5.15
Anthracene ($C_{14}H_{10}$)	2858.56	68.86	4.92
Phenanthrene ($C_{14}H_{10}$)	2864.15	74.45	5.32
Pyrene ($C_{16}H_{10}$)	3205.46	93.74	5.00
3,4-Benzanthracene ($C_{18}H_{12}$)	3631.80	90.75	5.04
Tetracene ($C_{18}H_{12}$)	3631.60	90.55	5.00
Triphenylene ($C_{18}H_{12}$)	3639.48	98.43	5.00
Chrysene ($C_{18}H_{12}$)	3638.60	97.55	5.00
Perylene ($C_{20}H_{12}$)	3969.50	106.10	5.31

[a] Pedley and Rylance (1977).

TABLE XXX

STABILIZATION ENERGIES OF HYDROCARBONS CONTAINING PHENYL GROUP(S) (IN KCAL MOL^{-1})

Compound	$\Delta H_a^{0\,a}$	SE^0	ESE^0
Styrene	1748.70	31.66	0.47
cis-Stilbene	2957.47	61.12	−1.26
trans-Stilbene	2961.66	65.31	2.93
Biphenyl	2528.23	60.88	−1.50
Diphenylmethane	2810.10	62.70	0.32
Triphenylmethane	4015.90	90.52	−3.05
Tetraphenylmethane	5219.40	114.60	−10.16
Indene	1915.89	26.49	−4.70
Acenaphthene	2534.40	42.60	−8.90[b]
Biphenylene	2363.11	2.41	−59.97

[a] Pedley and Rylance (1977).

[b] Calculated as: SE^0(acenaphthene) − SE^0(naphthalene).

delocalization and to steric repulsion, if any. Subtracting from each SE^0 the stabilization energy of benzene ring(s), we reveal specific interactions between the various groups in the molecule under consideration. The so-defined "extrastabilization energies" (ESE^0) show that these interactions are generally small. The large negative ESE^0 values of acenaphthene and especially biphenylene may be interpreted in terms of angular strain.

The stabilization and extrastabilization energies of a large variety of substituted benzenes have been calculated. In the case of monosubstituted species, it is found that electron-withdrawing substituents slightly decrease the stabilization energy (except NO_2, which corresponds to a relatively large negative ESE^0: −7.14 kcal mol^{-1}) and electron-releasing groups slightly increase it (NH_2 has the larger effect: $ESE^0 = 4.59$ kcal mol^{-1}). For disubstituted benzenes, the joint influence of substituents may be summarized as follows (see also Table XXXI):

	Electron withdrawing	Electron releasing
Electron releasing	$ESE^0_{\text{meta}} \leq ESE^0_{\text{para}}$	$ESE^0_{\text{para}} < ESE^0_{\text{meta}}$
Electron withdrawing	$ESE^0_{\text{meta}} \ll 0$	$ESE^0_{\text{meta}} \leq ESE^0_{\text{para}}$

It is clearly seen that the sign of ESE^0 does not depend on the character of the groups but on their nature and their position.

TABLE XXXI

EXTRASTABILIZATION ENERGIES OF DISUBSTITUTED BENZENES (IN KCAL MOL^{-1})

Compound	ΔH^{0}_{a}[a]	ESE^{0}
m-$C_6H_4(NO_2)_2$	1685.23	−14.58
o-$C_6H_4I_2$	1224.72	−5.77
o-$C_6H_4Cl_2$	1284.42	−5.45
m-$C_6H_4Cl_2$	1285.50	−4.37
p-$C_6H_4Cl_2$	1286.26	−3.61
o-$C_6H_4Cl(COOH)$	1682.52	−3.30
o-$C_6H_4(CH_3)_2$	1883.90	−2.19
m-$C_6H_4(COOH)(OCH_3)$	2069.28	−1.22
o-$C_6H_4(NO_2)(NH_2)$	1667.87	−0.64
p-$C_6H_4(COOH)(OCH_3)$	2070.69	0.19
p-$C_6H_4(NO_2)(NH_2)$	1668.90	0.39
p-$C_6H_4Cl(COOH)$	1686.34	0.52
m-$C_6H_4(NO_2)(NH_2)$	1669.14	0.63
p-$C_6H_4(CH_3)(OH)$	1702.62	0.75
m-$C_6H_4Cl(COOH)$	1686.63	0.81
o-$C_6H_4(OCH_3)_2$	2060.72	1.49
o-$C_6H_4(CH_3)(OH)$	1703.39	1.52
m-$C_6H_4(CH_3)(OH)$	1704.28	2.41
p-$C_6H_4(OH)_2$	1520.55	2.90
p-$C_6H_4(OCH_3)(CHO)$	1951.57	3.53
p-$C_6H_4(NH_2)(COOH)$	1864.13	4.64
m-$C_6H_4(OH)_2$	1517.65	5.12
p-$C_6H_4Cl(OH)$	1409.23	5.47
m-$C_6H_4Cl(OH)$	1411.02	7.26

[a] Pedley and Rylance (1977).

The ESE^0 values of monosubstituted benzenes reveal electronic effects of substituents, but those of disubstituted benzenes can be attributed to various causes:

1. Electronic effects in the case of meta and para derivatives.
2. Electronic and steric effects in the case of ortho-disubstituted benzenes. It is found that ESE^0 values of ortho compounds are most often negative and systematically lower than those of meta and para isomers, whatever the nature of the substituents may be.
3. Finally, electronic, eventually steric, and electrostatic effects in the case of halogenobenzenes. The ESE^0 values of those compounds are always negative and may be very large for perhalogeno derivatives (ESE^0 of C_6Cl_6 = −25.83 kcal mol^{-1}).

We must also point out the large destabilization of polynitrobenzenes (ESE^0 of 1,3,5-trinitrobenzene = -27.43 kcal mol^{-1}). Furthermore, it is seen that the effects of substituents are not additive (ESE^0 of p-$NH_2C_6H_4COOH \simeq ESE^0$ of $C_6H_5NH_2$).

In fact, from the energetic point of view, electronic effects of substituents are often less important than is generally thought. Moreover, contrary to common opinion, they may have an (electronic) destabilizing effect on the benzene ring.

i. Nonalternant hydrocarbons and heterocyclic aromatic compounds. As shown in Table XXXII, nonalternant hydrocarbons are much less stabilized than the corresponding alternant ones (if any). However, it must be pointed out that their SE^0 probably contains a destabilizing contribution due to angular strain. On the other hand, pyrrole, furan, and thiophene, having a relatively large stabilization, deserve the name "aromatic compounds."

4. *Some Peculiar Applications*

a. The thermochemistry of free-radical reactions. We show now that the concept of stabilization energy allows us to rationalize the thermochemistry of various free-radical reactions. Using the semiempirical or experimental heats of formation previously given (see Tables XIII, XIV, and XV) or reported elsewhere (Leroy, 1983a), we have calculated the stabilization energies of a large variety of free radicals. The results obtained are collected in Tables XXXIII for "carbon-centered," XXXIV for "nitrogen-centered," and XXXV for "oxygen-centered" species, respectively.

The stabilization energies of free radicals may contain contributions due to steric and (or) electrostatic interactions between bulky and (or)

TABLE XXXII

STABILIZATION ENERGIES OF NONALTERNANT HYDROCARBONS AND HETEROCYCLIC AROMATIC COMPOUNDS (IN KCAL MOL^{-1})

Compound	$\Delta H_a^{0\,a}$	SE^0	SE^0/N_π
Acenaphthylene ($C_{12}H_8$)	2405.55	44.85	3.74
Fulvene (C_6H_6)	1290.50	2.46	0.41
Azulene ($C_{10}H_8$)	2056.70	18.35	1.84
Furan	959.88	14.87	2.48
Thiophene	930.16	21.75	3.63
Pyrrole	1031.22	24.32	4.05

[a] Pedley and Rylance (1977).

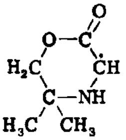
TABLE XXXIII

STABILIZATION ENERGIES OF CARBON-CENTERED FREE RADICALS (IN KCAL MOL^{-1})

Radical	SE^0	BDE(C—H)
$\dot{C}N$	−23.79	123.80
$HC{\equiv}\dot{C}$	−18.11	121.61
$\dot{C}Cl_3$	−18.02	96.15
$\dot{C}_6H_5$	−11.07	110.79
$\dot{C}_3H_5$	−8.06	106.25
$\dot{C}HCl_2$	−7.66	97.47
$\dot{C}H_2I$	−5.25	103.42
$\dot{C}H_2Br$	−4.58	102.49
$CH_2{=}\dot{C}H$	−2.27	103.05
$\dot{C}H_2F$	−2.16	101.00
$\dot{C}(CN)_3$	−2.02	68.23
$\dot{C}H_3$	−1.95	104.40
$\dot{C}H(OH)_2$	−1.94	100.53
$(CH_3)_3C\dot{C}HC(CH_3)_3$	−1.89[a] (−0.20[b])	94.11[c]
$\dot{C}H_2Cl$	−1.80	99.20
$\dot{C}H_2CH_3$	−0.50	100.48
$\dot{C}H_2CH_2CH_3$	−0.25	99.73
$\dot{C}H_2OH$	0.53	96.08
$\dot{C}H(CH_3)_2$	1.82	96.13
$CH_3\dot{C}HOH$	2.46	93.02
$\dot{C}H_2OCH_3$	2.64	94.08
$\dot{C}_6H_{11}$	3.42	94.57
$\dot{C}HF_2$	3.68	102.00
$\dot{C}(CH_3)_3$	3.70	93.92
$\dot{C}H_2NH_2$	4.53	93.60
$\dot{C}H_2CHO$	4.66	94.73
$\dot{C}H(CN)_2$	4.97	79.51
$(CH_3)_2\dot{C}OH$	5.01	90.13
$HO\dot{C}HCN$	6.32	81.95
$\dot{C}H_2CN$	6.60	92.98[d]
$\dot{C}H_2C{\equiv}CH$	10.56	89.00
$\dot{C}H_2C_6H_5$	10.81	87.93
$\dot{C}F_3$	10.98	105.80[e]
$[(CH_3)_2CHCH_2]_2\dot{C}CN$	12.07[f]	—
$C_6H_5\dot{C}(CH_3)_2$	11.81[g]	—
$H\dot{C}O$	12.06	87.08
$CH_2{=}CH\dot{C}HOH$	12.07	81.78
$(CH_3)_2\dot{C}CN$	12.18	86.04
$C_6H_5\dot{C}HCH_3$	12.53[g]	—
$\dot{C}H_2CH{=}CH_2$	12.91	86.67
$H_2N\dot{C}HCN$	13.30	80.79
$C_6H_5\dot{C}O$	13.67	87.44

(continued)

TABLE XXXIII (*Continued*)

Radical	SE^0	BDE(C—H)
$\dot{C}H_2C_{14}H_9$	13.94	84.79
$\dot{C}_5H_5$	14.27	81.74
$CH_3\dot{C}O$	14.72	86.33
$\dot{C}H_2C_{10}H_7$	15.15	83.22
$CH_2{=}CH\dot{C}HCH_3$	15.43	82.60
$CH_2{=}CH\dot{C}(CH_3)_2$	15.51	81.05
$C_6H_5\dot{C}(CN)(OCH_3)$	15.81[h]	—
$CH{\equiv}C{-}\dot{C}(CH_3)_2$	16.16	—
$\dot{C}H_2CF_3$	17.63	106.70
Cyclohexadienyl	20.22	75.80
	31.53[i]	65.41[i]

[a] Calculated from $\Delta H^{\ddagger}$ of the dissociation reaction (Rüchardt and Weiner, 1979):

$$[(CH_3)_3C]_3CH \rightarrow \dot{C}H[C(CH_3)_3]_2 + \dot{C}(CH_3)_3$$

[b] Calculated from $\Delta H^{\ddagger}$ of the dissociation reaction (Beckhaus *et al.*, 1978a):

$$[(CH_3)_3C]_2CHCH[C(CH_3)_3]_2 \rightarrow 2\dot{C}H[C(CH_3)_3]_2$$

[c] Cox and Pilcher (1970).

[d] An and Mänsson (1983).

[e] Rodgers *et al.* (1974).

[f] Calculated from $\Delta H^{\ddagger}$ of the reaction (Barbe *et al.*, 1983):

$$[(CH_3)_2CHCH_2]_2(CN)C{-}C(CN)[CH_2CH(CH_3)_2]_2 \rightarrow 2[(CH_3)_2CHCH_2]_2\dot{C}CN$$

[g] Robaugh and Stein (1981).

[h] Calculated from $\Delta H^{\ddagger}$ of the dissociation reaction (Rüchardt and Beckhaus, 1983):

$$C_6H_5(CN)(OCH_3)C{-}C(OCH_3)(CN)C_6H_5 \rightarrow 2C_6H_5\dot{C}(CN)(OCH_3)$$

[i] Calculated from BDE(C—C) = 22 kcal mol^{-1} (Bennett *et al.*, 1980) and ΔH_f^0 (dimer) estimated using our bond energy terms. BDE(C—H) is determined from ΔH_f^0 (parent molecule) estimated again using our bond energy terms. One finds: $\Delta H_f^0(R{-}R) = -206.87$, $\Delta H_f^0(R^{\cdot}) = -92.44$, and $\Delta H_f^0(RH) = -105.75$ kcal mol^{-1}.

TABLE XXXIV

STABILIZATION ENERGIES OF
NITROGEN-CENTERED FREE RADICALS
(IN KCAL MOL^{-1})

Radical	SE^0	BDE(N—H)
$\dot{N}C_4H_4$(cyclo)	−11.93	102.20[a]
$\dot{N}(CN)_2$	−9.80	90.51
$\dot{N}H_2$	−7.42	105.10
$\dot{N}HCH_3$	−4.15	96.90
$\dot{N}(CH_3)_2$	−3.72	94.00
$\dot{N}HNO_2$	−3.18	96.20
$\dot{N}(OH)(CN)$	1.14	72.73
$\dot{N}(CH_3)(CN)$	1.33	91.47
$\dot{N}HCN$	1.55	96.42
$\dot{N}HOH$	2.20[b]	90.13
$\dot{N}(OH)(NO_2)$	5.89	66.95
$\dot{N}HF$	6.07	86.50
$\dot{N}(NH_2)(CN)$	7.32	82.03
$\dot{N}HNH_2$	8.55[b]	82.26
$\dot{N}O_2$	10.30	66.00[c]
$\dot{N}HC_6H_5$	10.53	86.40
$\dot{N}(C_6H_5)_2$	12.64[d]	79.90
$\dot{N}F_2$	13.52	75.50
$\dot{N}(OH)_2$	15.35	76.23
$\dot{N}(NH_2)_2$	15.41	74.03
$\dot{N}O$	31.65	49.90[e]

[a] Cox and Pilcher (1970).
[b] Calculated from the data of Table XVI.
[c] Benson (1978).
[d] Kaba and Ingold (1976b).
[e] Benson (1976).

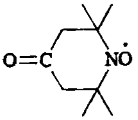
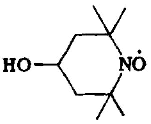
polar groups. Such interactions are very likely present in trichloro and tricyanomethyl radicals. However, in most cases, these SE^0 values essentially measure unpaired electron delocalization energies. Thus, it is not surprising to observe a close relation between stabilization energies and electronic properties of free radicals. Indeed, localized species are more or less destabilized and delocalized ones are often much stabilized.

Furthermore, the concept of stabilization energy allows us to characterize more quantitatively the various types of free radicals (Leroy, 1983b).

σ-Localized radicals are true *atom-centered* species. The spin density at the radical center and the corresponding isotropic hyperfine splitting

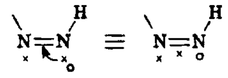
TABLE XXXV

STABILIZATION ENERGY OF OXYGEN-CENTERED FREE RADICALS (IN KCAL MOL^{-1})

Radical	SE^0	BDE(O—H)
$\dot{O}H$	−5.62	119.30
$\dot{O}C(CH_3)_3$	2.97	105.17
$\dot{O}CH_3$	4.06	104.11
$\dot{O}OH$	13.96	87.70
$\dot{O}OCH_3$	14.86	90.10
$\dot{O}C_6H_5$	24.26	86.52
	28.44	71.89
$\dot{O}NH_2$[a]	30.86	77.26
	33.06	65.00

[a] Calculated from the data of Table XVI.

constant are very large. Moreover, the Lewis octet and the Linnett double-quartet rules are not satisfied for this atom. The unpaired electron is said to be localized in an orbital with considerable s-character. σ-Localized radicals are generally destabilized. However, $HN\dot{N}$, which corresponds to a small BDE(N—H) [BDE(N—H) ≃ 60 kcal mol^{-1}], is anticipated to have a relatively large stabilization energy due to its important NN bond order as qualitatively described by the formulas:



Some typical examples of this first type of radical include the following species.

1. Carbon-centered species: $\dot{C}\equiv N$, $\dot{C}\equiv CH$, $\dot{C}H{=}CH_2$, $\dot{C}H{=}NH$, $\dot{C}_6H_5$, $\dot{C}Cl_3$, $\dot{C}_3H_5$, $\dot{C}H(OH)_2$. We must point out that the $\dot{C}F_3$ radical, although σ-localized, is largely stabilized as the corresponding parent molecule, CHF_3 (see Table XXI).
2. Nitrogen-centered species: $\dot{N}{=}CH_2$, $\dot{N}{=}NH$, $\dot{N}C_4H_4$ (cyclo).

π-Localized radicals are also atom-centered species. They are generally planar. Thus, their unpaired electron is in a pure p orbital and can only be delocalized by a mechanism of hyperconjugation. The following species belong to this class.

1. Carbon-centered radicals: unsubstituted alkyls and cyclohexyls:

$$-2 \le SE^0 \le 4 \quad \text{kcal mol}^{-1}$$

2. Nitrogen-centered radicals: $\dot{N}H_2$, $\dot{N}H(CH_3)$, $\dot{N}(CH_3)_2$:

$$-8 \le SE^0 \le -3 \quad \text{kcal mol}^{-1}$$

3. Oxygen-centered radicals: $\dot{O}H$, $\dot{O}C(CH_3)_3$, $\dot{O}CH_3$:

$$-6 \le SE^0 \le 4 \quad \text{kcal mol}^{-1}$$

σ-Delocalized radicals may be much stabilized, for their unpaired electron can be delocalized into adjacent lone pair(s). We find in this class

Carbon-centered radicals: $H\dot{C}O$, $C_6H_5\dot{C}O$, $CH_3\dot{C}O$:

$$12 \le SE^0 \le 15 \quad \text{kcal mol}^{-1}$$

π-Delocalized radicals are stabilized by a mechanism of spin delocalization, which can be interpreted in terms of usual conjugation effects. These species are essentially methyl, aminyl, and hydroxyl radicals substituted by unsaturated (vinyl, aryl) or functional groups (electron releasing, d; or electron withdrawing, c). For each type of π-delocalized radical, the following order of increasing stabilization energy is observed.

1. Substituted methyl radicals:

$c\,\dot{C}H_2 < C_6H_5\dot{C}H_2 < \dot{C}H_2{=}CH{-}CH_2$ $\qquad 6 \le SE^0 \le 13$ kcal mol^{-1}

$cc\,\dot{C}H < cd\,\dot{C}H$ $\qquad 4 \le SE^0 \le 32$ kcal mol^{-1}

2. Substituted aminyl radicals:

$c\,\dot{N}H < d\,\dot{N}H$ $\qquad -4 \le SE^0 \le 11$ kcal mol^{-1}

$cc\,\dot{N} < cd\,\dot{N} < dd\,\dot{N}$ $\qquad -10 \le SE^0 \le 15$ kcal mol^{-1}

3. Substituted hydroxyl radicals:

$\dot{O}OH < \dot{O}OCH_3 < \dot{O}C_6H_5 <$ nitroxides $\qquad 14 \le SE^0 \le 33$ kcal mol^{-1}

It is seen that the most stabilized species are cd-substituted methyls, dd-substituted aminyls, and nitroxides. Furthermore, electron-releasing substituents stabilize more nitrogen- and oxygen-centered radicals than the corresponding carbon-centered species, but the latter are less destabilized by electron-withdrawing substituents than the former ones. In fact, only $\dot{C}(CN)_3$ is destabilized in the chosen series of carbon-centered radicals.

It is interesting to compare our definition of radical stabilization to previous ones proposed by Szwarc (1948), Benson (1965), and Rodgers *et al.* (1972). According to Szwarc, the resonance energy of an unsaturated radical is the heat of the following (isodesmic) reaction:

$$R_\pi\dot{C}H_2 + CH_4 \longrightarrow R_\pi CH_3 + \dot{C}H_3$$

It can be written:

$$\Delta H^0 = BDE(CH_4) - BDE(R_\pi CH_3) = RE(R_\pi\dot{C}H_2) \tag{92}$$

Generalized to any type of carbon-centered radical, this approach has led to use of C—H bond dissociation energies for estimating the unpaired electron delocalization energies of these species. As shown in Tables XXXIII, XXXIV, and XXXV, bond dissociation energies which, except for a constant, are equal to heats of reaction do not provide satisfactory resonance (or stabilization) energies of free radicals. Indeed, as stated before, a heat of reaction can never be used for determining any property of one of the species involved in that reaction.

According to Benson's definition, the stabilization energy of an unsaturated radical is the heat of reaction of an alternative isodesmic process involving the fully hydrogenated compound corresponding to that radical:

$$R_\pi\dot{C}H_2 + R_sCH_3 \longrightarrow R_s\dot{C}H_2 + R_\pi CH_3$$

Thus:

$$\Delta H^0 = BDE(R_sCH_3) - BDE(R_\pi CH_3) = SE(R_\pi\dot{C}H_2) \tag{93}$$

For the same reason as before, this procedure, which is otherwise limited to unsaturated species, is to be rejected.

Finally, noting that $BDE(R_sCH_3)$ is not significantly affected by changes in the alkyl moiety, Rodgers *et al.* proposed systematically choosing $R_s \equiv CH_3$ and generalizing the previous definitions to include dissociation reactions involving a C—X bond, where X is any atom or group. Then $SE(R_\pi\dot{C}H_2)$ is written:

$$SE(R_\pi\dot{C}H_2) = BDE(CH_3CH_2X) - BDE(R_\pi CH_2X) \tag{94}$$

The latter definition has the same deficiency as the Szwarc and Benson definitions.

Thus, we are convinced that our concept of stabilization energy remains the only well-defined and general criterion for estimating the intrinsic thermodynamical stabilization of any compound.

Moreover, it can also be used for rationalizing the thermochemistry of free-radical reactions. At first, it is easy to show that the R—X bond dissociation energy of a given molecule may be written as:

$$BDE(\text{R—X}) = \sum E_{\text{AB}}(\text{RX}) - \sum E_{\text{AB}}(\text{R}^{\cdot}) + SE^0(\text{RX}) - SE^0(\text{R}^{\cdot}) \quad (95)$$

So, for example,

$$BDE(\text{CNCH}_2\text{—H}) = \sum E_{\text{AB}}(\text{CH}_3\text{CN}) - \sum E_{\text{AB}}(\dot{\text{C}}\text{H}_2\text{CN}) + SE^0(\text{CH}_3\text{CN}) - SE^0(\dot{\text{C}}\text{H}_2\text{CN}) \quad (96)$$

Using the data previously given, one obtains (in kcal mol^{-1}):

$$BDE(\text{CNCH}_2\text{—H}) = 595.73 - 493.90 - 2.25 - 6.60 = 92.68 \quad (97)$$

We can also write, more simply,

$$BDE(\text{R—X}) = \Delta\sum E_{\text{AB}} + \Delta SE^0 \quad (98)$$

As $\Delta\Sigma\, E_{\text{AB}}$ is not constant in a series of compounds, R—X bond dissociation energy does not linearly depend on ΔSE^0 or, *a fortiori,* on $SE^0(\text{R}^{\cdot})$.

On the other hand, the heat of a radical transfer reaction,

$$\text{RX} + \text{Y}^{\cdot} \longrightarrow \text{R}^{\cdot} + \text{XY}$$

is written, in terms of stabilization energies,

$$\Delta H^0 = SE^0(\text{RX}) - SE^0(\text{R}^{\cdot}) + \Delta\sum E_{\text{AB}} - BDE(\text{X—Y}) \quad (99)$$

It is clearly seen that ΔH^0 also does not linearly depend on ΔSE^0. However, as shown in Table XXXVI, the exothermicity of the radical transfer reaction,

$$\text{RH} + \dot{\text{C}}\text{H}_3 \longrightarrow \text{R}^{\cdot} + \text{CH}_4$$

generally increases as ΔSE^0 becomes more negative. It is noticeable that the role of the stabilization energy of the parent molecule (RH) is as important as the role of the SE^0 of the radical itself. Moreover, if the Evans–Polanyi (1938) relation holds for these reactions, the above reasoning can also be applied to the corresponding activation energy.

Let us now consider the bond cleavage reaction:

$$\text{R—R} \longrightarrow 2\text{R}^{\cdot}$$

The enthalpy change of this process is the so-called R—R bond dissociation energy [BDE(C—C) if R is an alkyl group].

TABLE XXXVI

RELATION BETWEEN $SE^0(\mathrm{R—H}) - SE^0(\mathrm{R}^\cdot)$ AND THE EXOTHERMICITY OF THE REACTION $\mathrm{RH} + \dot{\mathrm{C}}\mathrm{H}_3 \rightarrow \mathrm{R}^\cdot + \mathrm{CH}_4$ (IN KCAL MOL^{-1})

RH	$\mathrm{R}^\cdot$	$SE^0(\mathrm{R—H}) - SE^0(\mathrm{R}^\cdot)$	ΔH^0
CH_2F_2	$\dot{C}HF_2$	4.10	−2.30
$CHCl_3$	$\dot{C}Cl_3$	2.22	−8.85
CH_2Cl_2	$\dot{C}HCl_2$	1.83	−6.93
$CH_2(CN)(OH)$	$\dot{C}H(CN)(OH)$	−13.51	−22.45
$CH_2(CN)(NH_2)$	$\dot{C}H(CN)(NH_2)$	−15.71	−23.61
$CH_2(CN)_2$	$\dot{C}H(CN)_2$	−18.33	−24.89

For the reverse reaction (radical recombination), we obviously have

$$\Delta H^0(\text{recombination}) = -\Delta H^0(\text{bond cleavage}) = -BDE(\mathrm{R—R}) \quad (100)$$

or, more simply,

$$\Delta H_r^0 = -\Delta H_d^0 = -BDE(\mathrm{R—R}) \quad (101)$$

The following relations are easy to deduce:

$$BDE(\mathrm{R—R}) = E(\mathrm{R—R}) + SE^0(\mathrm{R—R}) - 2SE^0(\mathrm{R}^\cdot) \quad (102)$$

$$\Delta H_r^0 = 2SE^0(\mathrm{R}^\cdot) - SE^0(\mathrm{R—R}) - E(\mathrm{R—R}) \quad (103)$$

The latter allows us to rationalize the thermochemistry of radical dimerizations. $E(\mathrm{R—R})$ is the bond energy term corresponding to the bond in formation. It is seen that $BDE(\mathrm{R—R})$ (and $-\Delta H_r^0$) would be strictly equal to $E(\mathrm{R—R})$ if the radical and its dimer would be neither stabilized nor destabilized. Thus $E(\mathrm{R—R})$ may be considered as a standard bond dissociation energy. It allows us to define a reference reaction path for each couple of recombination–thermolysis processes. The deviation of an actual reaction path from the reference one depends on the stabilization energies of the species under consideration (Leroy, 1983a,b). Some standard bond dissociation energies are listed in Table XXXVII. The corresponding actual BDE values are given, respectively, by the following formulas:

$$BDE(\mathrm{C—C}) = 85.05 + SE^0(\mathrm{R_1R_2R_3CCR_1R_2R_3}) - 2SE^0(\mathrm{R_1R_2R_3\dot{C}}) \quad (104)$$

$$BDE(\mathrm{N—N}) = 47.88 + SE^0(\mathrm{R_1R_2NNR_1R_2}) - 2SE^0(\mathrm{R_1R_2\dot{N}}) \quad (105)$$

$$BDE(\mathrm{O—O}) = 46.14 + SE^0(\mathrm{ROOR}) - 2SE^0(\mathrm{R\dot{O}}) \quad (106)$$

$$BDE(\mathrm{S—S}) = 61.99 + SE^0(\mathrm{RSSR}) - 2SE^0(\mathrm{R\dot{S}}) \quad (107)$$

TABLE XXXVII

STANDARD BOND DISSOCIATION ENERGIES (IN KCAL MOL^{-1})

Bond	Standard *BDE*
C—C	85.05
N—N	47.88
O—O	46.14
S—S	61.99

The preceding formalism calls for several comments.

1. BDE(R—R) does not measure the stabilization energy of the radical except if SE^0(R—R) is negligible.

2. The thermodynamic stability of 1 mol of a given radical may be defined with respect to the recombination reaction. Then, it is written as:

$$\Delta G^0 = 2SE^0(\mathrm{R}^{\cdot}) - SE^0(\mathrm{R{-}R}) - E(\mathrm{R{-}R}) - T\Delta S^0 \qquad (108)$$

In the case of carbon-centered free radicals, one obtains, assuming $\Delta S^0(300) = -40$ Gibbs,

$$\Delta G^0(300) = 2SE^0(\mathrm{R}^{\cdot}) - SE^0(\mathrm{R{-}R}) - 73.05 \quad \mathrm{kcal\ mol^{-1}} \qquad (109)$$

or

$$\Delta G^0(300) = -BDE(\mathrm{C{-}C}) + 12 \quad \mathrm{kcal\ mol^{-1}} \qquad (110)$$

Thus, for being thermodynamically stable, carbon-centered radicals should correspond to a very small BDE(C—C) [$\Delta G^0 = 8.0$ kcal mol^{-1} if BDE(C—C) = 4.0 kcal mol^{-1}] or to a very large value of $2SE^0(\mathrm{R}^{\cdot}) - SE^0(\mathrm{R{-}R})$. It can be anticipated that very few species fulfill this condition. Consequently, practically no free radical should be thermodynamically stable. In other words, each time the recombination occurs it should quantitatively give the dimer.

Finally, we may wonder whether the concepts of thermodynamic stabilization and kinetic stabilization are related one to the other. It is well known that most free radicals are transient, which means they are not kinetically stabilized. In other words, they recombine without activation energy and, correspondingly, their dimer dissociates also without activation energy. Thus,

$$\Delta H^{\ddagger}_{\mathrm{d}} = BDE(\mathrm{R{-}R}) \qquad (111)$$

This is the reason why bond dissociation energies are often determined from kinetic measurements. On the other hand, some radicals corresponding to sterically hindered dimers are persistent and may even be stable. According to Griller and Ingold (1976), persistence is principally a consequence of steric factors. These authors have actually given many convincing proofs of this assertion. Furthermore, according to Rüchardt (1980), steric factors would also influence the rate of the thermolysis reaction leading to carbon-centered radicals. It is reasonable to assume that sterically induced persistence is due to a nonnegligible activation barrier on the pathway of the recombination reaction.

Although not numerous, there exist persistent and even stable *unhindered* radicals. Typical examples of such species are small nitroxides (Chapelet-Letourneux *et al.*, 1965; Adamic *et al.*, 1971), hydrazyls (Balaban, 1981), phenoxy radical (Nonhebel *et al.*, 1979), and nitric oxide. Moreover, some persistent *unhindered* carbon-centered radicals are known. The following species may be mentioned: (1) aminodicyanomethyl radicals (de Vries, 1977; Heimer, 1977), which have approximately the same SE^0 as benzyl radicals (Leroy, 1983a); (2) tricyanomethyl radical, which is slightly destabilized and has a relatively low decay constant, $k = 4.810^6$ liter mol^{-1} sec^{-1} (Kaba and Ingold, 1976a). Furthermore, as shown in Table XXXVIII, various types of free radicals recombine with a nonnegligible activation energy.

Generalizing our interpretation of the sterically induced persistence, we assume the dimerization reaction of any persistent radical has a noticeable activation energy due to various factors (electronic and or steric) appearing not only in the radical itself but also in its dimer.

For analyzing more deeply the origin of free-radical persistence and the eventual activation barrier of their dimerization reactions, we have wondered whether the latter obey the Evans–Polanyi relation:

$$E_a = \alpha \Delta H^0 + \beta \tag{112}$$

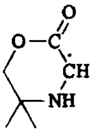
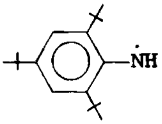
This seems actually to be the case for carbon-centered free radicals (Leroy, 1983a). Thus, generalizing this conclusion to any open-shell system, Eq. (112) may be written:

$$E_a = \alpha[2SE^0(\text{R}^\cdot) - SE^0(\text{R—R}) - E(\text{R—R})] + \beta \tag{113}$$

Equation (113) shows that the kinetic stabilization of a radical (as measured by E_a of its dimerization reaction) not only depends on its thermodynamic stabilization $[SE^0(\text{R}^\cdot)]$ but also on that of the corresponding dimer. Although the experimental data concerning free-radical reactions are generally not very accurate, we have used the data of Table XXXVIII

TABLE XXXVIII

ACTIVATION ENERGY OF THE RECOMBINATION REACTION OF SOME FREE RADICALS (IN KCAL MOL^{-1})

Radical	BDE(R—R)	$2SE^0(R^\cdot) - SE^0$(R—R)	E_a
$(C_6H_5)_2\dot{C}OH$	32.50	52.55	1.0[a]
	22.00	63.05	4.5[b]
$(F_3CS)_3\dot{C}$	13.70	71.35	7.3[c]
	13.10	34.78	2.5[d]
$(F_3CS)_2\dot{N}$	7.70	40.18	10.7[e]

[a] Weiner (1971).
[b] Bennett *et al.* (1980).
[c] Haas *et al.* (1979).
[d] Griller *et al.* (1975).
[e] Schlosser and Steenken (1983).

for estimating tentative numerical values for the constants α and β of Eq. (112). So one obtains, for C—C and N—N bond homolysis, respectively,

$$E_a = -0.337BDE(\text{C—C}) + 12.00 \quad \text{kcal mol}^{-1} \tag{114}$$

and

$$E_a = -1.519BDE(\text{N—N}) + 22.39 \quad \text{kcal mol}^{-1} \tag{115}$$

These activation energies are written more explicitly:

$$E_a = 0.337[2SE^0(\text{R}^\cdot) - SE^0(\text{R—R})] - 16.66 \quad \text{kcal mol}^{-1} \tag{116}$$

and

$$E_a = 1.519[2SE^0(\text{R}^\cdot) - SE^0(\text{R—R})] - 50.34 \quad \text{kcal mol}^{-1} \tag{117}$$

Some preliminary conclusions may be derived from the above equations. The persistence of free radicals is related to the bond dissociation energy of their dimer and, in this way, to $SE^0(\text{R}^\cdot)$ and SE^0(R—R). The dimerization reaction will have a nonnegligible activation energy if

BDE(R—R) is small [BDE(C—C) < 35; BDE(N—N) < 14 kcal mol^{-1}] or $2SE(\mathrm{R}^{\cdot}) - SE(\mathrm{R—R})$ is large [$2SE(\mathrm{R}^{\cdot}) - \mathrm{SE(R—R)} > 50$ for carbon-centered radicals and >33 kcal mol^{-1} for nitrogen-centered species].

Due to the negligible SE^0 of alkyl radicals, the *sterically induced persistence* of these species is clearly due to the large destabilization of their dimer. The persistence of *unhindered* species depends on both SE^0(R—R) and SE^0(R).

It is also interesting to note that Eq. (111) holds only if the activation energy of the recombination process is equal to zero, which corresponds to the following conditions (in the case of carbon radicals):

$$BDE(\mathrm{C—C}) > 35.6 \quad \mathrm{kcal\ mol^{-1}} \tag{118}$$

or

$$2SE(\mathrm{R}^{\cdot}) - SE(\mathrm{R—R}) < 49.5 \quad \mathrm{kcal\ mol^{-1}} \tag{119}$$

Otherwise, in general, $\Delta H_{\mathrm{d}}^{\ddagger}$ must be written as:

$$\Delta H_{\mathrm{d}}^{\ddagger} = BDE(\mathrm{C—C}) + E_{\mathrm{a}} \quad (\text{or } \Delta H_{\mathrm{r}}^{\ddagger}) \tag{120}$$

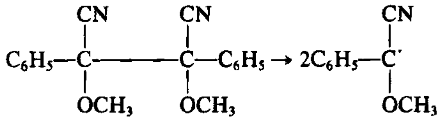
Therefore, if $\Delta H_{\mathrm{d}}^{\ddagger} < 35.6$ kcal mol^{-1} for a given homolysis reaction, it may be anticipated that the recombination reaction has a nonnegligible activation energy.

A useful relation may be deduced from Eqs. (120), (104), and (116):

$$\Delta H_{\mathrm{d}}^{\ddagger} = 68.39 - 0.663[2SE^0(\mathrm{R}^{\cdot}) - SE^0(\mathrm{R—R})] \tag{121}$$

This is only valid if $\Delta H_{\mathrm{d}}^{\ddagger} \leq 35.6$ kcal mol^{-1}. It allows us to determine $2SE^0(\mathrm{R}^{\cdot}) - SE^0(\mathrm{R—R})$ and so, to calculate BDE(C—C) and E_{a}. Moreover, if the heat of formation and therefore the stabilization energy of the dimer are known, one readily obtains the SE^0 and the heat of formation of the corresponding radical. The reverse is also obviously true. Three specific applications of Eq. (121) are given below:

(1)



$$\mathrm{C_6H_5—\overset{CN}{\underset{OCH_3}{C}}—\overset{CN}{\underset{OCH_3}{C}}—C_6H_5 \rightarrow 2C_6H_5—\overset{CN}{\underset{OCH_3}{C^{\cdot}}}}$$

$$\begin{aligned} \Delta H_{\mathrm{d}}^{\ddagger} &= 32.1 \quad \mathrm{kcal\ mol^{-1}} \\ \Delta H_{\mathrm{f}}^{0}(\mathrm{R—R}) &= 40.6 \quad \mathrm{kcal\ mol^{-1}} \\ SE^0(\mathrm{R—R}) &= -21.23 \quad \mathrm{kcal\ mol^{-1}} \end{aligned} \tag{122}$$

Thus:

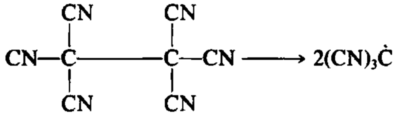
$$[2SE^0(\mathrm{R}^{\cdot}) - SE^0(\mathrm{R—R})] = 54.74 \quad \mathrm{kcal\ mol^{-1}} \tag{123}$$

Then it follows:

$$\begin{aligned} BDE(\mathrm{C{-}C}) &= 30.31 \quad \mathrm{kcal\ mol^{-1}} \\ E_a &= 1.79 \quad \mathrm{kcal\ mol^{-1}} \\ SE(\mathrm{R^{\bullet}}) &= 16.76 \quad \mathrm{kcal\ mol^{-1}} \\ \Delta H_f^0(\mathrm{R^{\bullet}}) &= 35.46 \quad \mathrm{kcal\ mol^{-1}} \end{aligned} \tag{124}$$

The latter results are original. They remain to be experimentally confirmed.

(2)



$$\mathrm{(CN)_3C{-}C(CN)_3 \longrightarrow 2(CN)_3\dot{C}}$$

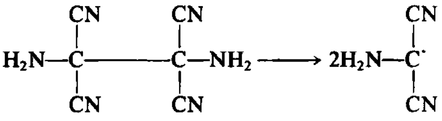
$$\begin{aligned} SE^0(\mathrm{R^{\bullet}}) &= -0.74 \quad \mathrm{kcal\ mol^{-1}} \\ SE^0(\mathrm{R{-}R}) &= 73.37 \quad \mathrm{kcal\ mol^{-1}} \\ 2SE^0(\mathrm{R^{\bullet}}) - SE^0(\mathrm{R{-}R}) &= 71.89 \quad \mathrm{kcal\ mol^{-1}} \\ \Delta H_f^0(\mathrm{R^{\bullet}}) &= 130.48 \quad \mathrm{kcal\ mol^{-1}} \end{aligned} \tag{125}$$

Thus, we readily obtain:

$$\begin{aligned} BDE(\mathrm{C{-}C}) &= 13.16 \quad \mathrm{kcal\ mol^{-1}} \\ E_a &= 7.57 \quad \mathrm{kcal\ mol^{-1}} \\ \Delta H_d^{\ddagger} &= 20.73 \quad \mathrm{kcal\ mol^{-1}} \end{aligned} \tag{126}$$

These are also original results which could explain the low decay rate constant of the tricyanomethyl radical.

(3)



$$\mathrm{H_2N{-}C(CN)_2{-}C(CN)_2{-}NH_2 \longrightarrow 2H_2N{-}C^{\bullet}(CN)_2}$$

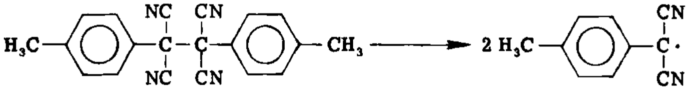
$$\begin{aligned} SE^0(\mathrm{R^{\bullet}}) &= 11.36 \quad \mathrm{kcal\ mol^{-1}} \\ SE^0(\mathrm{R{-}R}) &= -40.48 \quad \mathrm{kcal\ mol^{-1}} \\ [SE^0(\mathrm{R{-}R}) &\simeq 2SE^0(\mathrm{RH})] \\ 2SE^0(\mathrm{R^{\bullet}}) - SE^0(\mathrm{R{-}R}) &= 63.2 \quad \mathrm{kcal\ mol^{-1}} \end{aligned} \tag{127}$$

Thus it follows:

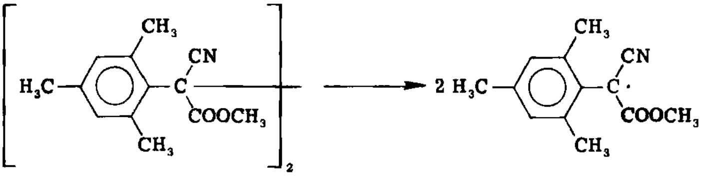
$$\begin{aligned} BDE(\text{C—C}) &= 21.85 \quad \text{kcal mol}^{-1} \\ E_a &= 4.64 \quad \text{kcal mol}^{-1} \\ \Delta H_d^{\ddagger} &= 26.49 \quad \text{kcal mol}^{-1} \end{aligned} \tag{128}$$

The persistence of the aminodicyanomethyl radical should be essentially due to the destabilization of its dimer, as that of $\dot{C}(CN)_3$. Electrostatic interactions between polar groups are presumably responsible for the large negative SE^0 values of the dimers.

Equations (104) and (121) can also be used for verifying the homogeneity of experimental data. We show below that the results obtained by Khudyakov *et al.* (1979) for two decomposition reactions do not seem very reliable.



$\Delta H_d^{\ddagger} = 15.9$ leads to $2SE^0(R^\cdot) - SE^0(R\text{—}R) = 79.17$ kcal mol^{-1}, and $BDE(\text{C—C}) = 9.1$, to the value of 75.95 kcal mol^{-1}.



$\Delta H_d^{\ddagger} = 15.2$ corresponds to $2SE^0(R^\cdot) - SE^0(R\text{—}R) = 80.23$ kcal mol^{-1}, and $BDE(\text{C—C})$, to the value of 72.65 kcal mol^{-1}.

The main conclusions of the preceding discussion are summarized in Table XXXIX. They show that the concept of stabilization energy allows us to rationalize the self-reactivity of free radicals (more particularly the carbon species for which more experimental data are available) and also the kinetic behavior of the corresponding dimers. The persistence of radicals may be due only to the stabilization energy of their dimer. This is the so-called sterically induced persistence and, also, that attributable to polar interactions in the dimer. In most cases the causes of persistence have a mixed origin: electronic stabilization of the radical and steric or polar destabilization of the dimer.

In our opinion, pure *electronic induced persistence* must be very rare because it would require an exceptional stabilization energy of the radical (~50 kcal mol^{-1}) and a negligible SE^0 of the corresponding dimer.

TABLE XXXIX

TENTATIVE RATIONALIZATION OF THE SELF-REACTIVITY OF CARBON-CENTERED FREE RADICALS (IN KCAL MOL^{-1})

$2SE^0(\text{R}^\cdot) - SE(\text{R—R})$	$BDE(\text{C—C})$	$\Delta H_d^\ddagger$	E_a	Character of R$^\cdot$
<50	>35	>35	0	Transient stabilized or not
>50	<35	<35	>0	Persistent stabilized or not
>80	<5	<5	>10	Stable, kinetically and thermodynamically stabilized

The activation enthalpy of the C—C bond homolysis can be identified to the *BDE*(C—C) except if the reaction leads to persistent radicals.

b. The stabilization energies of ionic species. The SE^0 values of a series of carbocations are collected in Table XL. They have been obtained using Eq. (81) with the data of Table XIII. We compare them with the corresponding heterolytic bond dissociation energies (*HBDE*) which are often used for estimating the stability of carbocations (Apeloig *et al.*, 1977). In fact, *HBDE* is the enthalpy change of the reaction:

$$\text{RH} \longrightarrow \text{R}^+ + \text{H}^-$$

It may be written:

$$HBDE = \Delta H_f^0(\text{R}^+) + \Delta H_f^0(\text{H}^-) - \Delta H_f^0(\text{RH}) \qquad (129)$$

or, in terms of stabilization energies,

$$HBDE = SE^0(\text{RH}) - SE^0(\text{R}^+) + \Delta \sum E_{\text{AB}} + I(\text{C}) - I(\text{H}^-) \qquad (130)$$

where $I(\text{C})$ and $I(\text{H}^-)$ are the ionization potentials of the carbon atom and hydride ion, respectively [$I(\text{C}) = 259.65$ kcal mol^{-1}; $I(\text{H}^-) = 17.4$ kcal mol^{-1} (Rosenstock *et al.*, 1977)]. In general, this quantity does not provide the correct order of carbocation stability, especially because of the nonnegligible stabilization energy of the RH molecule. However, as $\Delta \sum E_{\text{AB}}$ is approximately constant ($\Delta \sum E_{\text{AB}} \simeq 100$ kcal mol^{-1}), we must expect an approximate linear relationship between *HBDE* and the quantity $SE^0(\text{RH}) - SE^0(\text{R}^+)$. Inspection of Table XL shows that such a relation does actually exist. Its *a priori* expression is written as:

$$HBDE \simeq SE^0(\text{RH}) - SE^0(\text{R}^+) + 342 \quad \text{kcal mol}^{-1} \qquad (131)$$

It is seen that all the carbocations considered here have a positive SE^0. However, the species containing one or two CN groups are destabilized

TABLE XL

Stabilization Energies of Some Carbocations (in kcal mol^{-1})

Carbocation	*HBDE*	SE^0(RH)	$SE^0(R^+)$
$\overset{+}{C}H(CN)_2$	317.67	−13.36	9.07
$F\overset{+}{C}HCN$	312.44	−8.22	19.39
$\overset{+}{C}H_2CN$	311.89	0.00	29.95
$\overset{+}{C}H_3$	313.91	4.20	30.79
$\overset{+}{C}H_2F$	291.01	0.00	50.10
$HO\overset{+}{C}HCN$	272.72	−7.19	57.81
$\overset{+}{C}HF_2$	284.84	7.91	63.03
$\overset{+}{C}F_3$	294.81	21.66	64.83
$\overset{+}{C}H_2{-}CH{=}CH_2$	256.73	0.00	85.05
$\overset{+}{C}H_2OH$	251.78	0.00	86.98
$\overset{+}{C}H(CH_3)_2$	251.34	0.00	88.87
$\overset{+}{C}H_2OCH_3$	236.70	0.00	102.29
$H_2N\overset{+}{C}HCN$	233.33	−2.41	103.02
$\overset{+}{C}(CH_3)_3$	233.32	0.83	106.55
$\overset{+}{C}H(OH)_2$	225.21	6.06	116.15
$\overset{+}{C}H_2NH_2$	218.21	0.00	122.18
$\overset{+}{C}H_2NHCH_3$	205.14	−0.08	134.74
$\overset{+}{C}H_2N(CH_3)_2$	198.38	−0.08	141.28

with respect to $\overset{+}{C}H_3$. Thus, in general, as commonly assumed, electron-withdrawing substituents exert a destabilizing effect on the corresponding carbocation, and electron-donating groups, a stabilizing effect. A more systematic study of carbocations (Leroy *et al.*, 1983d) provides the following order of stabilization energies for the species containing only one type of substituent:

$$\overset{+}{C}H_2CF_3 < \overset{+}{C}H_2CHO \leq \overset{+}{C}H_2CN < \overset{+}{C}H_3 < \overset{+}{C}F_3 < \overset{+}{C}H_2F < \overset{+}{C}HF_2$$

$$\overset{+}{C}H_2CH_3 < \overset{+}{C}H_2{-}CH{=}CH_2 < \overset{+}{C}H_2OH < \overset{+}{C}H(CH_3)_2 < \overset{+}{C}H_2OCH_3$$

$$< \overset{+}{C}(CH_3)_3 < \overset{+}{C}H_2NH_2 < \overset{+}{C}H_2NHCH_3 < \overset{+}{C}H_2N(CH_3)_2 < \overset{+}{C}H(NH_2)_2$$

As expected, the best π-donor groups have the most stabilizing effect.

The stabilization energies of a few negative ions are given in Table XLI. They have been calculated using Eq. (82) with the data of Table

TABLE XLI

STABILIZATION ENERGIES OF SOME NEGATIVE IONS (IN KCAL MOL^{-1})

Ion(R^-)	$\Delta H^0_{ac.}$(RH)[a]	SE^0(RH)	SE^0(R^-)
CH_3^-	416.1	4.20	−29.48
$CH_3CH_2^-$	(405.4)[b]	0.00	−21.03
CCl_3^-	376.1	−15.80	−14.15
$CH_2{=}CH{-}CH_2^-$	390.8	0.00	−3.72
$C_6H_5CH_2^-$	379.0	−1.03	1.78
$(HO)(CN)CH^-$	371.4	−7.19	7.29
$C_6H_5^-$	(374.0)[b]	0.00	10.33
$CNCH_2^-$	372.2	0.00	11.97
$C_5H_5^-$	356.1	−2.21	26.14
F_3C^-	375.6	21.66	28.05
CN^-	353.1	−3.50	34.98
$(CN)_2CH^-$	336.0	−13.36	35.84

[a] Leroy *et al.* (1981), and references therein.
[b] Value obtained for $(CH_3O)(CN)CH_2$.
[c] Estimated using Eq. (133).

XXXIII and the electron affinities of the corresponding radicals (Leroy *et al.*, 1981, and references therein). It is seen that all the substituents considered here stabilize CH_3^-. This shows they are all able to delocalize the negative charge, i.e., the lone pair of the carbon atom.

Some authors (Pross *et al.*, 1980) proposed to measure the stability of negative ions by means of their gas-phase acidity, which is nothing else but the enthalpy change of the reaction:

$$RH \longrightarrow R^- + H^+$$

It may be written in terms of stabilization energies:

$$\Delta H^0_{ac.}(RH) = SE^0(RH) - SE^0(R^-) + \Delta \sum E_{AB} - A(C) + I(H) \qquad (132)$$

where A(C) and I(H) are the carbon atom electron affinity and the hydrogen atom ionization potential, respectively. Thus, this quantity will not measure the stabilization energy of the negative ion under consideration except if SE^0(RH) is negligible, which is rarely the case. Nevertheless, an approximate linear relationship must exist between $\Delta H^0_{ac.}$(RH) and $SE^0(RH) - SE^0(R^-)$ as $\Delta\Sigma\, E_{AB}$ is approximately constant. Then, we can write:

$$\Delta H^0_{ac.}(RH) \simeq SE^0(RH) - SE^0(R^-) + 384.33 \quad \text{kcal mol}^{-1} \qquad (133)$$

TABLE XLII

INFLUENCE OF SUBSTITUENTS ON THE METHYL RADICAL AND ITS POSITIVE AND NEGATIVE IONS

Type	$SE^0(\dot{C}HXY) -$ $SE^0(\dot{C}H_3)$	$SE^0(\overset{+}{C}HXY) -$ $SE^0(\overset{+}{C}H_3)$	$SE^0(CHXY^-) -$ $SE^0(CH_3^-)$
$X = c; Y = H$	>0	<0	$\geqslant 0$
$X = d; Y = H$	>0	$\geqslant 0$	<0
$X = c; Y = d$	>0 to $\geqslant 0$	>0	>0

The gas-phase acidities, $\Delta H^0_{\text{ac.}}(\text{RH})$, are also listed in Table XLI. They satisfactorily obey Eq. (133). Thus, they may be used to guess $\Delta H^0_{\text{ac.}}(\text{RH})$ values not yet experimentally determined, from corresponding $[SE^0(\text{RH}) - SE^0(\text{R}^-)]$ values independently obtained.

We shall retain the following order of stabilizing influence for the substituents under consideration:

$$H < CH_3 < CH_2 = CH < C_6H_5 < CN$$

Moreover, the high stabilization energy of cyclopentadienyl anion (comparable with that of benzene: 31.19 kcal mol^{-1}) demonstrates the aromatic character of this species, in agreement with the $4n + 2$ Hückel rule.

The influence of substituents on $\dot{C}H_3$, $\overset{+}{C}H_3$, and CH_3^- is summarized in Table XLII, according to their type (captor, c; donor, d).

IV. The Reactivity of Chemical Species

A. Introduction

The ultimate goal of quantum chemistry is the rationalization and the prediction of the reactivity of chemical species. It may be reached by the various approaches briefly described in Sections I and III and summarized in Fig. 14.

Considering an elementary process involving only one or two molecules and assuming it may be described by a series of stationary solutions of the time-independent Schrödinger equation, we are led to search the wave function Γ of the corresponding supermolecule by solving Eq. (1). When the separation of electronic and nuclear motions is allowed, the wave functions of the two types of particles can be obtained independently from Eqs. (4) and (5).

If the electronic equation is solved for a wide variety of nuclear configurations, one obtains the potential energy hypersurface of the supermole-

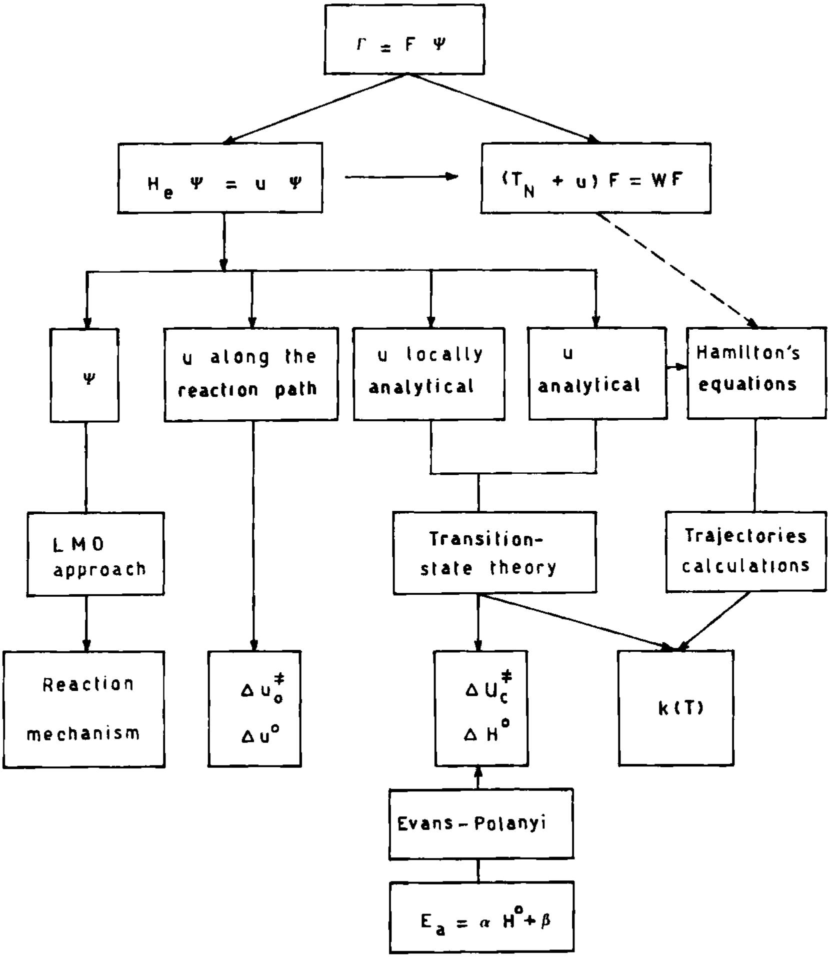


Fig. 14. Summary of the main theoretical approaches to chemical reactivity.

cule under consideration. Such calculations can only be accurately performed for small systems. They provide detailed information on the reaction path (activation barrier and energy of reaction at 0 K) and the mechanism of the corresponding reaction. The thermodynamic parameters of this reaction may be obtained from the energy levels of the equilibrium structures of reactants and products, theoretically estimated by solving the nuclear equations of these species. The kinetic parameters and the rate constant of the reaction can be evaluated within the framework of the *transition-state theory* or by performing *classical trajectories calculations*.

Indeed, as the resolution of the nuclear Schrödinger equation can only be performed for very simple systems, one can often use a classical approach where nuclei are no longer considered as quantum particles but as classical ones moving on the potential energy hypersurface. Then, we may calculate reaction probabilities which are related to the reaction rate constant by an equation deduced in statistical mechanics. This can be formally written:

$$k(T) = \int \text{probabilities} \times \text{density of states} \tag{134}$$

Thus, the kinetic parameters can also be deduced in this approach.

If we are interested in "medium-size" supermolecules, the hypersurface can be locally computed with a good accuracy. In that case, we no longer obtain the reaction path, but the kinetic parameters and the rate constant can again be calculated using the formalism of transition-state theory.

For large supermolecules, we can only obtain approximate potential energy hypersurfaces, most often at the SCF level using small basis sets and considering a limited number of structural parameters. Thus we calculate only the portion of the hypersurface which is expected to contain the reaction pathway. The heats of reaction and activation barriers obtained by this approach are generally not very accurate. Moreover, thermal and ZPE corrections cannot be performed due to the lack of analytic expression of the surface. However, this approach provides a detailed description of the nuclear displacements along the reaction path and the reorganization of the electron pairs of the supermolecule during the corresponding chemical process. So, one obtains interesting information on the so-called reaction mechanism.

Finally, as shown in Section III, empirical relations such as the one proposed by Evans and Polanyi allow us to rationalize different types of chemical reactions and even, in favorable cases, to make interesting predictions.

In this section, we chiefly summarize the main results obtained in the theoretical study of elementary processes involving large supermolecules.

B. The Theoretical Study of Reaction Mechanisms

1. *Preliminary Remarks*

We have studied a wide variety of organic reactions involving a large supermolecule. In every chosen reaction, the number of electron pairs is conserved such that the correlation energy remains roughly constant during the process. Thus, most of the calculations have been performed at the SCF level using the STO-3G basis set. Moreover, only the portion of the hypersurface which is supposed to contain the reaction path has been calculated in each case.

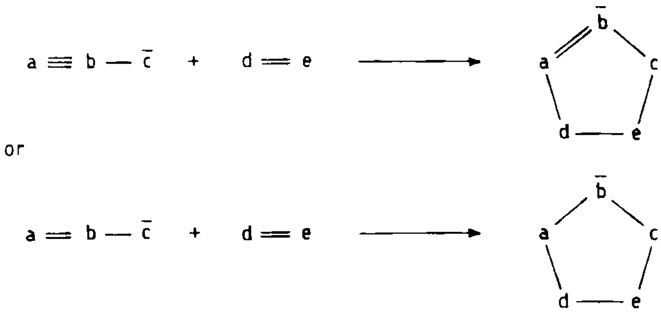
We have been particularly interested in the description of the energetic, geometric, and electronic properties of the supermolecule along the reaction pathway. The originality of our work lies in the careful study of the evolution of the LMO's centroids of charge during the reaction. As shown before, these centroids approximately coincide with the centers of charge of two-electron (pseudo)loges. Thus, their evolution allows us to demonstrate the reorganization of the electron pairs of the supermolecule during its transformation and, therefore, to determine the mechanism of the corresponding chemical reaction. The detailed results of our work may be found elsewhere (Leroy *et al.*, 1980, and references therein). Then, in the following discussion, we shall concentrate on the electronic mechanisms we have determined.

2. *1,3-Dipolar Cycloadditions*

These reactions are described by the general equation:

1,3-dipole + dipolarophile → five-membered heterocycle

According to Huisgen (1963), a 1,3-dipole is a compound isoelectronic with either propargyl anion, $[\mathrm{CH{\equiv}CH{-}\bar{C}H_2}]^-$, or allyl anion, $[\mathrm{CH_2{=}CH{-}\bar{C}H_2}]^-$, being linear and bent species, respectively. On the other hand, the dipolarophile is an unsaturated compound. Thus, the above equation can be more explicitly written:



where a, b, and c may be CH_2, CH, NH, N, or O, for example.

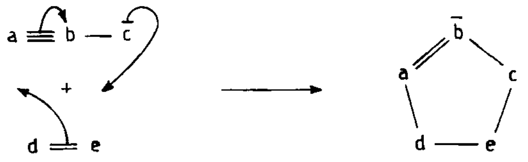
Many experimental data are in favor of a concerted mechanism but the two-step mechanism proposed by Firestone (1968, 1972) seems to deserve yet serious attention (Hiberty *et al.*, 1983). The methodology we have adopted allows us only to explore that portion of the potential energy hypersurface which corresponds to the concerted approach. Thus our results will support neither Huisgen's nor Firestone's mechanism but they will allow us to determine the mechanism of the concerted approach.

Let us consider first the geometrical results. We have found that the coplanar approach of the reactants which maintains all heavy atoms in the same plane is systematically favored in the case of linear dipoles. On the other hand, the so-called parallel approach is favored with bent dipoles. At the transition state, the mean distance between centers a and d or c and e is slightly larger than 2 Å, as shown below for various atom couples (S is the standard deviation):

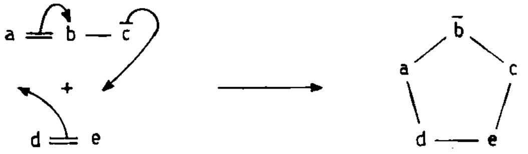
C—C	$\bar{d} = 2.28$ Å	$S = 0.07$ Å
C—N	$\bar{d} = 2.16$ Å	$S = 0.08$ Å
C—O	$\bar{d} = 2.19$ Å	$S = 0.06$ Å
N—N	$\bar{d} = 2.05$ Å	$S = 0.09$ Å
N—O	$\bar{d} = 2.07$ Å	$S = 0.05$ Å

Considering then the electronic point of view, we have found that the charge transfer, at the transition state, is always rather small and takes place, in most cases, from the dipole toward the dipolarophile. Moreover, the analysis of the evolution of the centroids of charge along the reaction path demonstrates that all concerted 1,3-dipolar cycloadditions proceed from a cyclic movement of three π-electron pairs as shown in Fig. 15 for two typical reactions involving a linear and a bent dipole, respectively.

Thus, the electronic mechanism of concerted 1,3-dipolar cycloadditions is now well established. It may be written with the usual notations of organic chemists:



or



Moreover, we have shown that the direction of electron pair migration is determined by the charges of the terminal atoms of the reactants: the new bonds start from the most negative ends of the molecules. This result is very useful for rationalizing the regiochemistry of these reactions and the influence of substituents on the reactivity of the dipole and the dipolarophile (Leroy *et al.*, 1980, and references therein; Daudel *et al.*, 1983).

Let us finally consider the energetic results. It is well known that heats of reaction and activation barriers calculated at the SCF-STO-3G level are

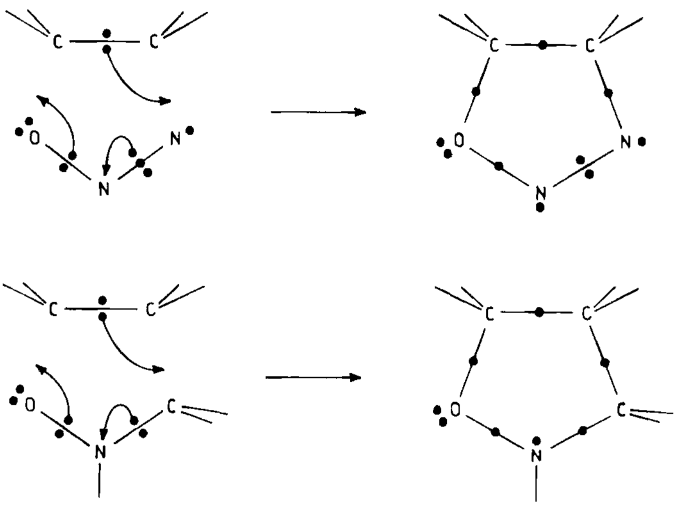
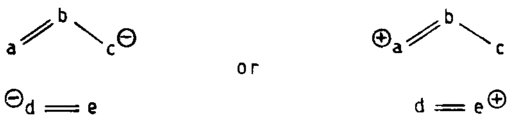


Fig. 15. Evolution of the centroids of charge in two typical 1,3-dipolar cycloadditions involving a linear and a bent dipole, respectively.

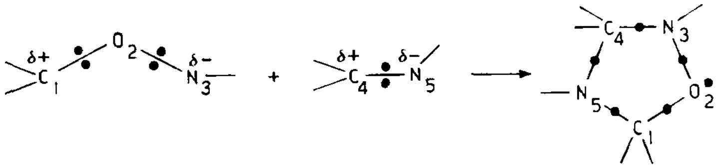
not very accurate. The theoretical heats of reaction of the 41 1,3-dipolar cycloadditions we have studied are in fact systematically overestimated. However, the activation barriers are pretty well correlated with the corresponding available activation energies.

One will also note that among the two possible approaches of the reactants, the most favored one (that corresponding to the smallest activation barrier, i.e., the so-called normal addition) is described as:



This result allows us to propose a new definition of the normal addition: it is the reaction which leads to the product corresponding to the above approach. This is characterized by a complementary electrostatic disposition of the dipole and the dipolarophile.

Furthermore, we may also propose original synthesis of heterocycles such as:



Finally, a multivariate statistical analysis of our theoretical results has been recently performed (Sana *et al.*, 1982) in order to determine the leading factors responsible for the activation energy of 1,3-dipolar cycloadditions. It is found that the relation which best explains the activation barrier of the chosen reactions is written:

$$\Delta u_0^{\ddagger} = 0.027\Delta E - 11.9q_d - 14.1q_e + 67.6q_b - 396q_a + 0.113E_{de} - 0.230E_{bc} + 0.180E_{ab} - 1.29\mu_{de} + 3.59\mu_{abc} \qquad (135)$$

where ΔE is the theoretical heat of reaction; q_i, the net charge of atom i; E_{ij}, the semiempirical bond energy of bond ij (Leroy and Sana, 1976); and μ, the theoretical dipole moment of a given molecule (abc or de).

It is seen that the lowest activation barrier is obtained when the following requirements are simultaneously met:

1. ΔE largely negative (Evans–Polanyi relation).
2. q_a positive.
3. q_e more positive than q_d.
4. E_{de} as small as possible (ethylenic dipolarophiles have a larger reactivity than acetylenic ones).
5. E_{ab} small and E_{bc} large (the reactivity of linear dipoles is smaller than that of bent dipoles).

The rather small activation barrier of concerted cycloadditions involving bent dipoles leads us to exclude the two-step mechanism for these reactions. On the other hand, the quite large activation barrier of the cycloadditions involving linear dipoles would be in favor of the conclusion of Hyberty *et al.*, i.e., for those reactions "quite probably both mechanisms compete . . . ."

In conclusion, our results concerning 1,3-dipolar cycloadditions allow us to rationalize a wide variety of experimental data and to propose a general mechanism describing both the nuclear and electronic motions responsible for these reactions.

3. *Cycle-Chain Isomerizations*

The thermal isomerization of 1,5-dipoles (1,3-dipoles substituted by an unsaturated group) leads to various five-membered heterocycles, as shown in Fig. 16. Using the same procedure as before, we have determined the mechanism of the thermal cyclization of propargyl-type species derived from HN_3, i.e., azidoazomethine (d=e ≡ CH=NH) and vinylazide (d=e ≡ $CH=CH_2$).

We have demonstrated that the ring closure of azidoazomethine proceeds from the migration of four electron pairs, just after the transition

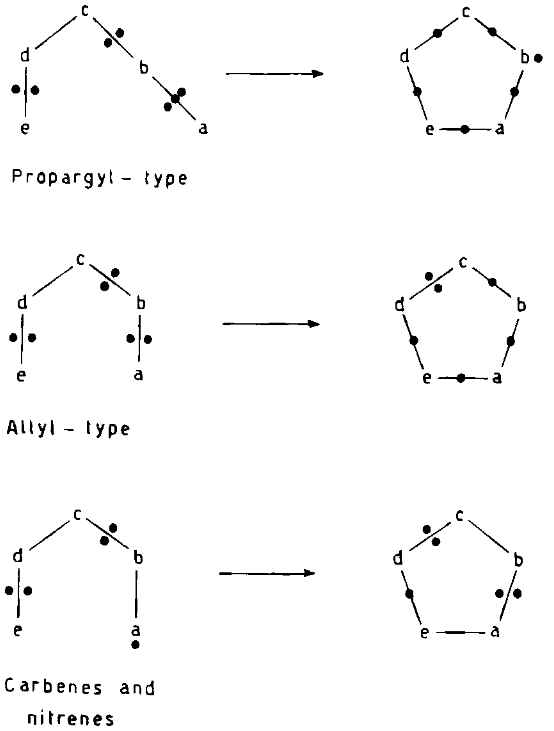
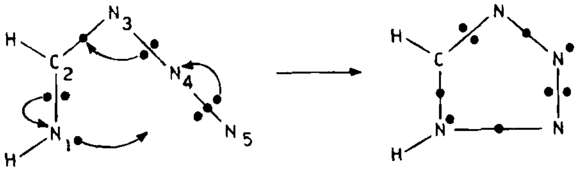


Fig. 16. Ring closure of 1,5-dipoles.

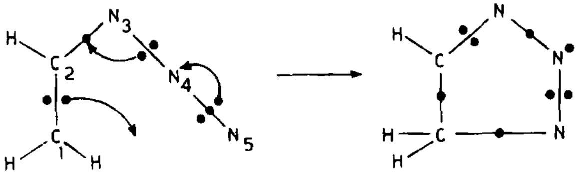
state (Burke *et al.*, 1976). This reorganization is described in Fig. 17. The keynote of this process is the presence of a lone pair on nitrogen N_1 which permits the formation of the new σ bond without having to rotate the NH group around the C_2N_1 double bond.

This result, which is completely general, explains the relatively small activation energy of the ring closure of 1,5-dipoles where "e" represents an atom or group having such a lone pair ($\overline{N}R$ or $\overline{O}|$). We can also anticipate that the factors which increase the availability of this lone pair will favor the cyclization process. On the other hand, the protonation of e would prevent the ring closure.

The vinylazide–triazole isomerization is in fact very similar to the cyclization of azidoazomethine in acidic media. We have found (Burke *et al.*, 1978) that these reactions proceed from the displacement of three electron pairs, one of them being the π-electron pair of the C_1C_2 double bond. This electronic reorganization is also shown in Fig. 17. The large activation energy of these ring closures is merely due to the rupture of the π system by turning the CH_2 or NH_2^+ terminal group.



8 electrons involved



6 electrons involved

Fig. 17. Electronic mechanism of the ring closure of azidoazomethine and vinylazide.

Thus cycle-chain isomerizations of 1,5-dipoles involve the migration of eight or six electrons according to whether the center e has a lone pair or not. These conclusions may be generalized to any type of 1,5-dipole without performing other computations.

4. *Reactions Involving Medium-Size and Small Supermolecules*

We are also interested in the theoretical study of reactions involving smaller supersystems. So, we are now considering elementary processes concerning open-shell species such as (1) hydrogen-abstraction reactions corresponding to medium-size supermolecules and (2) the various transformations of the small supersystem DHF.

The electronic mechanism of the former reactions has been determined using the LMO approach, and their kinetic parameters and rate constant have been calculated within the framework of the transition-state theory. A detailed description of our preliminary results is given elsewhere (Leroy, 1981; Villaveces, 1981; Daudel *et al.*, 1983; Sana *et al.*, 1984). We shall only recall here the main conclusions they suggest.

The UHF procedure is accurate enough to determine optimized geometries and to perform vibrational analysis. However, configuration interaction is needed for calculating the energetic properties of isolated species and activated complexes. To handle the problem of selecting configurations in a truncated CI, the diagonalization perturbation iterative technique [CIPSI; Huron *et al.* (1973)] within an iterative natural orbital (INO) scheme and with an extrapolation for estimating the energies corresponding to a full CI appears to be a very effective procedure.

An important remark is now to be made. Even though it is interesting to be able to reproduce experimental data such as heats of reaction, activation energies, and rate constants, this is not the main goal of the theoretical approach to chemical reactivity. In fact, we want rather to rationalize experimental data by providing information on properties which cannot be measured, such as those of a transition structure. Therefore, in this field as in most other fields of quatum chemistry, theory and experiment are essentially complementary.

Furthermore, in spite of its preliminary character, this work allows us to propose an electronic mechanism for hydrogen-abstraction reactions from methane. This may be written as:

$$H_3C \uparrow\!\downarrow H + \uparrow R \rightarrow \left[H_3C \uparrow \overset{\delta+}{H} \downarrow \ \uparrow \overset{\delta-}{R}\right]^{\ddagger} \rightarrow H_3C \uparrow + H \downarrow \ \uparrow R$$

The driving force of this reaction is found to be the electron affinity of the attacking radical.

Finally, this work demonstrates the capability of the transition-state theory to provide accurate rate constants of chemical reactions, at least at temperatures at which tunneling plays a relatively negligible role.

Our theoretical approach to the DHF supersystem is now in progress (Reckinger, 1983). The first results yet obtained may be found elsewhere (Sana *et al.*, 1981; Daudel *et al.*, 1983; Sana, 1983).

V. General Conclusions

We have seen that the formalism of quantum chemistry allows us to approach many chemical problems related to the structure and reactivity of chemical species. Various points of view and approximation levels can be adopted depending on the nature and the size of the problem to be solved.

General theorems and postulates enable us to find the physical interpretation of chemical phenomena. Therefore, classical theories and qualitative concepts may be criticized and, consequently, either rejected or confirmed and generalized. Considering the physical nature of the chemical bond, we have seen that the correct meaning and the limitations of Lewis' ideas are clearly specified by this quantum-mechanical approach. So, it is now well demonstrated that *the formation of a covalent bond results from the concentration of (paired) electrons in the internuclear region leading to a strong binding force and a concomitant decrease of the mean electronic potential energy*. This result is particularly interesting from a pedagogical point of view, i.e., for correctly teaching the electronic theory of valence.

Explicit calculations are often needed for solving chemical problems. In this work, we have adopted a point of view which is quite different from that of the qualitative or quantitative MO theory extensively used for many years by theoretical and even experimental chemists.

Our LMO approach to the electronic structure and reactivity of chemical species allowed us not only to generalize the (Lewis and Linnett) theory of valence but also to determine the mechanism of a wide variety of organic reactions.

We have also proposed a general definition of the concept of stabilization energy applying to any compound, as shown by the numerous applications described in this survey article. Using this concept, we have been able to carry out a critical analysis and to offer a unified definition of various former notions such as hyperconjugation, resonance, ring strain, and steric repulsion energies.

Moreover, a detailed classification of free radicals has been derived from their stabilization energies and their electronic structure obtained by the LMO approach. We have shown that the self-reactivity of these species is not only related to their above properties but also to the corresponding ones of their dimer. We recall the main formulas we have deduced for comparing the thermodynamic and kinetic stabilization of free radicals:

$$E_a = -\alpha BDE(\mathrm{R{-}R}) + \beta$$

or, as

$$BDE(\mathrm{R{-}R}) = E(\mathrm{R{-}R}) + SE^0(\mathrm{R{-}R}) - 2SE^0(\mathrm{R}^\cdot)$$

$$E_a = \alpha[2SE^0(\mathrm{R}^\cdot) - SE^0(\mathrm{R{-}R})] + k$$

These formulas provide an interpretation of the transience or persistence of radicals and lead to a clear definition of these concepts.

Furthermore, an explicit expression of the activation enthalpy of alkane homolysis has also been found. It is written as:

$$\Delta H_d^\ddagger = 68.39 - 0.663[2SE^0(\mathrm{R}^\cdot) - SE^0(\mathrm{R{-}R})]$$

if

$$BDE(\mathrm{C{-}C}) < 35.6 \quad \mathrm{kcal\ mol^{-1}}$$

and

$$\Delta H_d^\ddagger = 85.05 - [2SE^0(\mathrm{R}^\cdot) - SE^0(\mathrm{R{-}R})]$$

if

$$BDE(\mathrm{C{-}C}) > 35.6 \quad \mathrm{kcal\ mol^{-1}}$$

The above formulas allow us to rationalize the experimental data concerning the thermal dissociation of alkanes and the corresponding free-radical recombinations. Interesting predictions of various thermodynamic and kinetic parameters of these reactions can also be made.

Finally, the stabilization energies of ionic species may be related to some properties of the corresponding molecules such as their heterolytic bond dissociation energy (*HBDE*) and their gas-phase acidity ($\Delta H^0_{\mathrm{ac.}}$).

Thus, the joint utilization of theoretical and experimental results enables one to solve chemical problems of relatively great complexity.

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Modern Aspects of Diatomic Interaction Theory

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> *Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry—an aberration which is happily almost impossible—it would occasion a rapid and widespread degeneration of that science.* [A. Comte, Philosophie Positive]

I. Introduction

A. Overview

More than 20 and 10 years have passed since the publication of two well-known books, "Spectra of Diatomic Molecules" by G. Herzberg and "Diatomic Interaction Potential Theory" by J. Goodisman, respectively, which are devoted to the problem of diatomic potential energy functions, or, in other words, the theory of diatomic interactions. Time after time excellent and superior reviews have appeared, and we can refer to the literature of Varshni, Stwalley, Le Roy, Carney, Kolos, Winn, and others. However, their number is not so many. The theory of diatomic interactions occupies the simplest position within the general theory of intermolecular interactions, for which there remain many theoretical problems. Unsolved problems also concern the theory of diatomic interactions, and the "Everest" of the complete understanding of the nature of diatomic interactions remains unsubjugated!

Probably, the reader thinks that the authors, by analogy, denote the preferable way to Everest's peak. This is not the case; here the goal consists in reviewing the modern state of the art of diatomic interaction theory and discussing the currently available tools for the mountaineering, and the reader must continue in pursuit of the peak without the authors' assistance, after reading the review presented. To facilitate the reader–mountaineer, the structure of this review article is provided in the following overview.

Section I is devoted to the general foundations of diatomic interaction theory. In the next section, some power-series expansion approaches are discussed for the adequate representation of diatomic interaction in the neighborhood of its potential minima. This is followed in Section III by a study of the short-range behavior of diatomic interactions. Section IV is devoted to some approaches, mainly semiclassical, for solving the Schrödinger equation to obtain the vibrational–rotational spectra of diatomics and related problems, such as finding Regge poles of a given diatomic potential and the coherent state of diatomics. In Section V the Padé approximants and their application to the study of diatomic interactions are examined. Presented in Sections VI–VIII are the force and energetic pictures of diatomic potential energy functions based on the well-known famous theorems in quantum chemistry, the virial and the Hellmann–Feynman theorems. In Section IX the momentum-space aspect of diatomic interactions is treated, which provides a new picture complementary to the ordinary picture in position space. The manner of the description of diatomic interactions in the framework of the density functional theory is considered in Section X, followed in the next section by a powerful mathematical way to obtain diatomic potential functions from experimental data. Therefore, this article is written basically with emphasis on the mathematical* aspect of the theory of diatomic interactions. Nevertheless, some of the emphasis, as in Sections VII and IX, for example, is on the more physical and interpretative aspects. The reason is clear: these sections deal intimately with such concepts as "force" and "charge distribution," which are sufficiently intelligible to bridge mathematics and physics.

B. Background

For the theory of diatomic interactions, the number of reviews (Nielsen, 1951; Varshni, 1957; Vanderslice and Lippincott, 1962; Ruedenberg, 1962; Wahl and Das, 1970; Le Roy, 1973; Stwalley, 1973a; Carney *et al.*, 1978; Le Roy and Carley, 1980; Winn, 1981; Murrell *et al.*, 1982) and books (Gaydon, 1947; Herzberg, 1950; Wilson *et al.*, 1955; Slater, 1963; Hirschfelder *et al.*, 1964b; Margenau and Kestner, 1971; Goodisman, 1973; Vol'kenstein *et al.*, 1973; Mulliken and Ermler, 1977; Gribov, 1980; Kaplan, 1982) is rather limited. In the authors' opinion, the reason for this apparently lies in the fact that although this is the simplest type of intermolecular interaction, all the complexity of intermolecular interactions is reflected, as in a drop of water, in its nature.

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* Equations are numbered in each section. If reference is made in one section to an equation in another section, the section number is included, e.g., Eq. (II.6).

What do diatomic interactions themselves represent? What is their nature? Do there exist means for their approximations with the help of not so complex analytical expressions? What is the physical sense, if it exists, of the parameters in such expressions? How do they reproduce the real interactions and their corresponding characteristics? And so on. In the theory of diatomic interactions there exist a large number of questions which await steps to their final solutions.

Let us consider a system AB consisting of two atoms, A and B, with the nuclear charges Z_A and Z_B, respectively. The interaction between these atoms is described by a function $U(R)$, where R is the distance between the nuclei. Within the framework of the Born–Oppenheimer approximation,

$$U(R) = Z_A Z_B / R + W(R) \tag{1}$$

where $W(R)$ is the total energy of the electronic subsystem.

The function $U(R)$ is denoted as the diatomic potential energy function. Usually it is represented by a curve (see Fig. 1) and characterized by

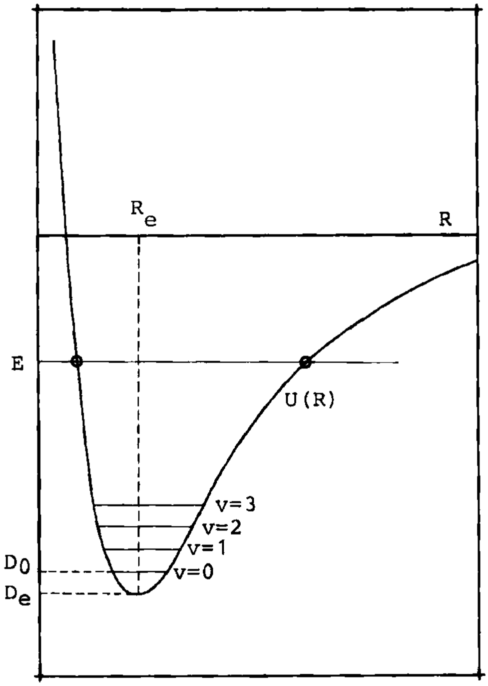


Fig. 1. Typical diatomic interaction potential curve. Turning points corresponding to the energy level E are denoted by circles.

the following quantities (unless otherwise stated, atomic units are used throughout this article):

1. The equilibrium internuclear distance $R = R_e$. (It is assumed that at least one minimum exists, i.e., the system AB is assumed to be stable.)

2. The value of the total electronic energy at $R = R_e$,

$$E_e^0 \equiv W(R_e) \tag{2}$$

and D_e defined by

$$D_e \equiv E_e^0 + Z_A Z_B / R_e \equiv U(R_e) \tag{3}$$

which determines the depth of the potential well.

3. The dissociation energy D_0, which is the difference between the electronic energy at the infinite nuclear separation and the total energy of the zeroth vibration. D_0 is distinguished from D_e by the value of the zeroth vibration

$$D_e = D_0 + \tfrac{1}{2}\omega_e \tag{4}$$

There exists a striking empirical law which relates R_e with ω_e

$$R_e^2 \omega_e = \text{const.} \simeq 2.7 \tag{5}$$

for all diatomics. This simple law was first discovered by Birge and Mecke (Birge, 1925; Mecke, 1925). More recently, this law has been discussed by Borkman and Parr (Borkman and Parr, 1968) and Ohwada (Ohwada, 1982a,b).

4. The harmonic force constant

$$k^{(2)} \equiv d^2 U/dR^2|_{R=R_e} \tag{6a}$$

or the Sutherland parameter

$$\Delta \equiv k^{(2)} R_e^2 / 2D_e \tag{6b}$$

5. The higher order anharmonic force constants

$$k^{(n)} \equiv d^n U/dR^n|_{R=R_e}, \qquad n = 3, 4, \ldots \tag{6c}$$

Sometimes the following notations are adopted:

$$K_e = k^{(2)}, \qquad L_e = k^{(3)}, \qquad M_e = k^{(4)}, \qquad N_e = k^{(5)}, \qquad \text{etc.} \tag{6d}$$

All the force constants reflect the shape of the potential well. It is evident that the potential well with the same D_e can possess, in principle, quite different shapes, from a very narrow to a very broad one.

6. The dispersion series near the dissociation limit. As $R \to \infty$, $U(R)$ has the following asymptotic behavior (Ahlrichs, 1976; Buckingham,

1978; Claverie, 1978):

$$U(R) \simeq \sum_{n=n_0} C_n/R^n \tag{7}$$

where n_0 depends on the nature of the bonding for a given diatomic molecule. The first term in Eq. (7), C_{n_0}/R^{n_0}, is often denoted as the leading term.

In items 1–6, the purely geometrical or static characteristics of $U(R)$ are presented. However, $U(R)$ possesses also the energetic or dynamical peculiarities. One of them, D_0, was defined in item 3. Therefore, solving the Schrödinger equation with the potential

$$U_{\text{eff}}(R, J) = U(R) + J(J + 1)/(2\mu R^2) \tag{8}$$

where J is an angular momentum and μ is the reduced nuclear mass, one can obtain, in principle, the following dynamical characteristics:

7. The eigenfunctions and the eigenenergies of the Hamiltonian of the system AB with the potential given by Eq. (8). The eigenfunctions and the eigenenergies, belonging to the discrete spectrum of the Hamiltonian, are enumerated by the numbers v and J. The value $v = 0$ at $J = 0$ corresponds to the lowest energy state, where v is the vibrational quantum number. Notice that v is not always an integer (ter Haar, 1946). Then the Dunham formula takes place,

$$E(v, J) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} Y_{ij}(v + \tfrac{1}{2})^i [J(J + 1)]^j \tag{9}$$

where $E(v, J)$ is the energy of the vibration–rotation level characterized by v and J.

8. If $J = 0$, the following standard notations are used ($j = 0$):

$$\begin{aligned} &Y_{00} = D_e, \qquad Y_{10} = \omega_e, \qquad Y_{20} = -\omega_e x_e \\ &Y_{30} = \omega_e y_e, \qquad Y_{40} = -\omega_e z_e, \qquad \text{etc.} \end{aligned} \tag{10}$$

where Y_{i0} ($i \geq 1$) may be derived from the force constants arising in the Taylor expansion of $U(R)$ around $R = R_e$. For example,

$$\omega_e x_e = \{(\tfrac{5}{3})[k^{(3)}/k^{(2)}]^2 - k^{(4)}/k^{(2)}\}(W/\mu) \tag{11}$$

where $W = 2.1078 \times 10^{-16}$.

9. Similarly, if $J \neq 0$, there follows from Eq. (9) the well-known expression for the energy of the vibrating rotator;

$$\begin{aligned} E(v, J) = E(v, J = 0) &+ B_v[J(J + 1)] - D_v[J(J + 1)]^2 \\ &+ H_v[J(J + 1)]^3 + L_v[J(J + 1)]^4 + \cdots \end{aligned} \tag{12}$$

where

$$B_v = B_e - \alpha_e(v + \tfrac{1}{2}) + \gamma_e(v + \tfrac{1}{2})^2 + \cdots, \qquad \text{etc.} \tag{13}$$

and

$$B_e = 2\pi\hbar/(8\pi^2 c\mu R_e^2) = h/(8\pi^2 c I_e) \tag{14}$$

$$\alpha_e = -(6B_e^2/\omega_e)[1 + (2k^{(3)}/3k^{(2)})R_e] \tag{15}$$

with B_e being the rotational constant and I_e the inertia moment.

10. Each vibrational level v is characterized by its turning points, $R_{\min}(v)$ and $R_{\max}(v)$, where the vth energy level intersects the curve $U(R)$, i.e.,

$$E(v, J = 0) = U(R_{\min}(v)) = U(R_{\max}(v)) \tag{16}$$

and

$$R_{\min}(v) < R_e < R_{\max}(v)$$

It is evident that the concept of the turning points is purely classical. Nevertheless, it has appeared to be very fruitful in the semiclassical study of diatomic interactions. The set of the turning points for a given diatomic potential reflects sharply its form and is very useful in the construction procedure of a suitable empirical diatomic potential curve.

11. Each (v, J) level of the vibration–rotation spectrum is also characterized, in addition to its turning points, by its minimum $R_e(J)$. Recently, Craven, Murrell, and Varandas (Craven *et al.*, 1982) proposed an algorithm for finding $R_e(J)$ for $U_{\text{eff}}(R, J)$ with an arbitrary $J \leq J_c$, where J_c corresponds to that critical value of J above which the given potential $U_{\text{eff}}(R, J)$ has no minima. They imposed the following assumptions:

$$dR_e(J)/dJ|_{J=0} = 0, \qquad dR_e(J)/dJ|_{J=J_c} = \infty \tag{17}$$

The generally accepted concept of molecular structure and molecular geometry is directly connected with the adiabatic postulate of Born and Oppenheimer. This postulate provides an introduction to the notation of the equilibrium geometry for each minimum of the electronic energy as a function of the internuclear separation. In a particular case of diatomic molecules, such a dependence of the electronic energy is represented by a two-dimensional graph which is usually called the diatomic potential energy curve. The study of such curves in terms of the characteristics, accepted in the molecular vibrational theory, just accounts for the subject of the theory of diatomic interactions. In the framework of this theory, any chemical bonding, for example, covalent, polar, or ionic, is characterized by a definite set of quantities—so-called molecular vibrational-rotational constants, which are mentioned above. Therefore, the existence of chemical bonding in a given diatomic system and hence the chemical bonding itself may be characterized by some set of quantities. However, the set proposed by Aroca and Robinson (1982), which consists of R_e, ω_e, $k^{(2)}$, and D_0, is obviously incomplete.

In summary, we note that in the beginning of the present section we assumed that the potential curve possesses at least one minimum. Nevertheless, the potential curves may have no minima. This leads to the instability of the system. And, vice versa, they may also have more than one minimum. In general, the problem of the number of minima is not so simple (see Clinton, 1963).

II. Diatomic Potential Series Expansions

Power-series expansions of a diatomic potential energy function are the most useful means for its analytical representation, which allows, on one hand, adequate description of a given diatomic potential, and, on the other hand, connection of diatomic interactions to spectroscopy. Working in the framework of this approach, one needs essentially to specify the region of convergence for a given power-series expansion. Then we have the range of its validity, and need to be careful in the interpretation of results obtained. The problem of determining the region of convergence for a given power-series expansion is very difficult, in the analytical plan, and, naturally, depends essentially on the analytical expression of the power-series expansion examined. In particular, the region of convergence is found for simple analytical expressions of the power-series expansion for ionic molecules (Finn and Beckel, 1960). In general, for real diatomic potentials, however, we are unaware of decreased radii of convergence caused by singularities off the real R-axis.

In recent years, more and more attention has been given to the problem of the most convenient and adequate representation of diatomic potentials via some types of analytical functions. It is evident that the general universal approach of such a representation should satisfy the following requirements (Varshni, 1957): (1) satisfy the general conditions imposed on the diatomic potential (see Section I); (2) provide the effective use of both limited and broad spectroscopic information, as well as the other data available such as scattering, thermophysical characteristics, etc.; (3) describe adequately the specific features of the different types of chemical bondings—ionic, covalent, polar, and van der Waals; and (4) give the correct asymptotic behavior for large internuclear separations.

In the present section we discuss the power-series expansions of diatomic potentials, and among these we consider in detail the expansions suggested by Dunham, Simons, Parr, and Finlan, Thakkar, Ogilvie and Tipping, and Engelke. Each of these approaches has advantages and disadvantages which, in the first place, are determined by the range of convergence. It is necessary to note that we must remember at all times that there exists no unique universal representation of diatomic potentials.

A. Dunham Power-Series Expansion

In 1932, Dunham proposed the following power-series expansion to represent a diatomic potential $U(R)$ about its minimum (Dunham, 1932):

$$U(\xi_D(R)) = U_e + a_0^D \xi_D{}^2 \left[1 + \sum_{n=1}^{\infty} a_n^D \xi_D^n\right] \qquad (1)$$

with

$$\xi_D = (R - R_e)/R_e \qquad (2)$$

and a_0^D and $a_0^D a_n^D$ ($n \geq 1$) are the Taylor series coefficients.

If R varies in $[0, \infty)$, then ξ_D ranges from -1 to $+\infty$. And there are no singularities in $\xi_D = \xi_D(R)$ in the finite complex R-plane. It is trivial. The domain of convergence of the Dunham expansion is not greater than $0 < R < 2R_e$ (Beckel and Engelke, 1968). Therefore, the Dunham expansion has a radius of convergence equal to R_e if there are no singular points on $U(R)$, Eq. (1), in the complex R-plane within the circle of radius R_e centered at the point $R = R_e$, i.e., one can say that this expansion is valid only in the region at the bottom of the well.

It is evident that the Dunham (or simply, D) series is completely determined by the whole set of its Taylor series coefficients $\{a_0^D, \{a_0^D a_n^D\}_{n=0}^{\infty}\}$. But in practice, there do not exist any methodics to permit the determination of all this set, and in fact only a few of the a_n^D are known. In the latter case, Eq. (1) is transformed to a low-order polynomial with respect to ξ_D, which has naturally the incorrect behavior as $\xi_D \to 0$, which corresponds to $R \to \infty$. In particular, Cashion (1966) noted that the D-coefficients higher than a_4^D are somewhat ambiguous in their meaning (see also Stwalley, 1973a). At the same time, even if only the a_n^D, for example, a_0^D, a_1^D, a_2^D, are known, the D-expansion provides a very accurate approximation for the real $U(R)$ near the equilibrium point $R = R_e$ (Kolos and Wolniewicz, 1964; Engelke, 1978). But the set of the D-coefficients has one difficulty in practical property, namely $|a_n^D|$ does not converge to zero as $n \to \infty$. To confirm this statement, we give the following results, obtained easily from the table of D-coefficients by Engelke (1978):

$$|a_0^D| = 0.205363273, \qquad |a_1^D| = 1.6886219, \qquad |a_2^D| = 2.063570$$

$$|a_3^D| = 2.28248, \qquad |a_4^D| = 2.4107$$

and

$$|a_1^{\mathrm{D}}/a_0^{\mathrm{D}}| = 8.222611, \qquad |a_2^{\mathrm{D}}/a_1^{\mathrm{D}}| = 1.222043$$
$$|a_3^{\mathrm{D}}/a_2^{\mathrm{D}}| = 1.106083, \qquad |a_4^{\mathrm{D}}/a_3^{\mathrm{D}}| = 1.056175$$

To avoid this problem, Engelke (1978) suggested the so-called Coulomb-subtracted D-expansion [CSD-expansion, which was first outlined by Wu and Beckel (1973)] of the following type:

$$U_{\mathrm{CSD}}(\xi_{\mathrm{D}}(R)) = U_{\mathrm{e}} + \beta^{\mathrm{D}}/(1 + \xi_{\mathrm{D}}) + \sum_{n=0}^{\infty} \tilde{a}_n^{\mathrm{D}} \xi_{\mathrm{D}}^n \tag{3}$$

where the following relations between $\{a_n^{\mathrm{D}}\}_{n=0}^{\infty}$ and $\{\beta^{\mathrm{D}}, \{\tilde{a}_n^{\mathrm{D}}\}_{n=0}^{\infty}\}$ hold:

$$\begin{aligned} &\tilde{a}_0^{\mathrm{D}} = -\beta^{\mathrm{D}}, \qquad \tilde{a}_1^{\mathrm{D}} = \beta^{\mathrm{D}}, \qquad \tilde{a}_2^{\mathrm{D}} = a_0^{\mathrm{D}} - \beta^{\mathrm{D}} \\ &\tilde{a}_n^{\mathrm{D}} = a_0^{\mathrm{D}} a_{n-2}^{\mathrm{D}} - (-1)^n \beta^{\mathrm{D}}, \qquad n > 2 \end{aligned} \tag{4}$$

Evidently, in Eq. (3) the term associated with the nuclear Coulomb repulsion, A/R, is added by Engelke. Then $\beta = A/R_{\mathrm{e}}$. This term has a simple pole at $R = 0$. If, moreover, we add the centrifugal potential of the type B/R^2 and write the modified Coulomb-centrifugal-subtracted D-expansion as

$$U_{\mathrm{CCSD}}(\xi_{\mathrm{D}}(R)) = U_{\mathrm{e}} + \beta^{\mathrm{D}}/(1 + \xi_{\mathrm{D}}) + \gamma^{\mathrm{D}}/(1 + \xi_{\mathrm{D}})^2 + \sum_{n=0}^{\infty} \tilde{\tilde{a}}_n^{\mathrm{D}} \xi_{\mathrm{D}}^n \tag{5}$$

then we have the second-order pole at $R = 0$. In the particular case of the CSD-expansion, the convergence property for $|\tilde{a}_n^{\mathrm{D}}|$ takes place. For $\tilde{a}_n^{\mathrm{D}}$ from Eq. (2), we have

$$\begin{aligned} &|\tilde{a}_1^{D}/\tilde{a}_0^{\mathrm{D}}| = 1, && |\tilde{a}_2^{\mathrm{D}}/\tilde{a}_1^{\mathrm{D}}| = 0.5898498 \\ &|\tilde{a}_3^{D}/\tilde{a}_2^{\mathrm{D}}| = 0.5211698, && |\tilde{a}_4^{\mathrm{D}}/\tilde{a}_3^{\mathrm{D}}| = 0.4997427 \\ &|\tilde{a}_5^{D}/\tilde{a}_4^{\mathrm{D}}| = 0.4155550, && |\tilde{a}_6^{\mathrm{D}}/\tilde{a}_5^{\mathrm{D}}| = 0.1762203 \end{aligned} \tag{6}$$

Representing a given diatomic potential as a power-series expansion in terms of the ξ_{D} variable, Eq. (1), Dunham justified via the WKBJ approach (see Section IV) the well-known energy expression for diatomic molecules (Dunham, 1932):

$$E(v, J) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} Y_{ij}(v + \tfrac{1}{2})^i [J(J + 1)]^j \tag{7}$$

where v is the vibrational quantum number, J the rotational quantum number, and the energy zero is chosen at $R = R_{\mathrm{e}}$. In this formula, v is an integer which is not the exact solution, but a very good approximation (ter Haar, 1946). This statement is general for all applications of the WKBJ approach. Kilpatrick (1959) rediscovered this equation, Eq. (7), with the help of the quantum-mechanical Rayleigh–Schrödinger perturbation theory. Dunham's formula, Eq. (7), was the first analytical expression which connected a form of diatomic potential with energetic characteristics of a molecule. In that, we see its fundamental property.

In Eq. (7) the coefficients Y_{ij} are constants, depending on R_e, $\{a_n^D\}_{n=0}^{\infty}$, and the reduced mass μ, with the μ-dependence of Y_{ij} being as follows:

$$Y_{ij} = \mu^{-(i/2+j)}[Z_{ij,0} + \mu^{-1}Z_{ij,1} + \mu^{-2}Z_{ij,2} + \cdots] \tag{8}$$

where the coefficients $Z_{ij,k}$ are functions of R_e and $\{a_n^D\}_{n=0}^{\infty}$ only. The inclusion of adiabatic and nonadiabatic corrections to Y_{ij} was examined in detail by Bunker (1970, 1972). And conversely, the $\{a_n^D\}_{n=0}^{\infty}$ are obtained from the Y_{ij}, which in turn are determined from experimental data. In common, one can obtain the Y_{ij} for lower values of $i + j$—in principle, for $i + j \leq 3$. Then one can obtain only nine Y_{ij}, from which six diatomic potential parameters, namely R_e, a_0^D, a_1^D, a_2^D, a_3^D, a_4^D, are obtained (Stwalley, 1973a).

Therefore we may conclude that the Dunham expression for vibrational–rotational eigenenergies, $E(v, J)$, is valid and useful only for levels lying in the region at the bottom of the well, as the analogous D-expansion, but it becomes useless as v increases, and, moreover, the Dunham formula diverges in the energy dissociation limit (Beckel and Engelke, 1968; Coolidge *et al.*, 1938; Beckel, 1976; Pekeris, 1934). It is necessary to add that in the framework of the Dunham approach the Schrödinger equation is not solved exactly and does not provide the exact analytical reproduction of wave functions.

In the Dunham approach, spectroscopic constants are expressed in terms of the D-coefficients [see Eq. (I.10)]:

$$\omega_e = 2(a_0^D B_e)^{1/2} = B_e/\beta \tag{9}$$

$$\alpha_e = -6B_e\beta(1 + a_1^D) \tag{10}$$

$$x_e = -(\tfrac{3}{2})\beta[a_2^D - (\tfrac{5}{4})(a_1^D)^2] \tag{11}$$

where $\beta = (\frac{1}{2})(B_e/a_0^D)^{1/2}$ serves as a measure of the contribution of the rotational energy terms relative to the vibrational energy terms. Calder and Ruedenberg (1968) carried out an interesting analysis of the behavior of spectroscopic constants for all diatomic molecules composed of atoms from a given pair of columns in the periodic table. The correlation rules discovered by them are very useful in the study of diatomic molecules.

B. Simons–Parr–Finlan Expansion

In 1973, Simons, Parr, and Finlan (SPF) proposed an alternative power-series expansion. They have chosen instead of $\xi_D(R)$ a new independent variable $\xi_{\mathrm{SPF}}(R) = (R - R_e)/R$ (Simons *et al.*, 1973; Finlan and Simons, 1975). The relation between ξ_{D} and ξ_{SPF} is as follows: $\xi_{\mathrm{D}} = \xi_{\mathrm{SPF}}/(1 - \xi_{\mathrm{SPF}})$. We obtain the Simons–Parr–Finlan power-series expansion if we replace $\xi_{\mathrm{D}}(R)$ in Eq. (1) with $\xi_{\mathrm{SPF}}(R)$. (Accordingly we must replace a_n^{D} with a_n^{SPF}.) It is evident that ξ_{SPF} lies in the interval $(-\infty, 1]$ for the R range of $[0, \infty)$, and the function $\xi_{\mathrm{SPF}}(R)$ is an analytical one in the complex R-plane except for the point $R = 0$. From this point of view, the SPF expansion has poles of all orders, and therefore it gives the incorrect representation of $U(R)$ at $R = 0$. There exist the direct relationships between the D- and the SPF-expansion, which in terms of corresponding coefficients are expressed as follows (Simons *et al.*, 1973; Finlan and Simons, 1975):

$$a_0^{\mathrm{D}} = a_0^{\mathrm{SPF}}, \qquad a_1^{\mathrm{D}} = a_1^{\mathrm{SPF}} - 2$$

$$a_n^{\mathrm{D}} = a_n^{\mathrm{SPF}} - \sum_{i=1}^{n-1} (-1)^i \binom{n+1}{i} a_{n-i}^{\mathrm{SPF}} + (-1)^n (n+1), \qquad n > 2 \qquad (12)$$

The SPF-coefficients do not satisfy the convergence property: as $n \to \infty$, $|a_n^{\mathrm{SPF}}/a_{n-1}^{\mathrm{SPF}}| \not\to 0$. In particular, from Eq. (12) and the D-coefficients derived by Engelke (1978) (see Section II,A), we obtain

$$|a_1^{\mathrm{SPF}}/a_0^{\mathrm{SPF}}| = 0.3113779, \qquad |a_2^{\mathrm{SPF}}/a_1^{\mathrm{SPF}}| = 0.007373451$$

$$|a_3^{\mathrm{SPF}}/a_2^{\mathrm{SPF}}| = 69.65874, \qquad |a_4^{\mathrm{SPF}}/a_3^{\mathrm{SPF}}| = 1.577053$$

In contrast to the D-approach, the truncated SPF-series has the correct behavior as $R \to \infty$. Nevertheless, the truncated SPF-expansion does not provide the correct reproduction of the behavior of $U(R)$ in the neighborhood of $R = 0$. For instance, if we truncate this series at $n = 1$, we obtain a third-order pole at $R = 0$, where the correct potential has a pole of the first order.

The SPF-approach appears to have given more accurate and correct results for diatomic systems than the D-version, in comparison of the experimental data (Carney *et al.*, 1976; Carney and Wolken, 1976). In particular, this is explained by in that the SPF-series gives better reproduction of $U(R)$ for $R \geq R_e$, as confirmed by Engelke (1978). He obtained, in both cases, that when a_0^{D} through a_2^{D}, and a_0^{D} through a_4^{D}, are known, the SPF-series is superior to the D- and CSD-series for $R \geq R_e$. One can prove this statement purely analytically.

As a result, the SPF-approach has a more predictive force than does the D-version. This argument provides the wide application of the SPF-approach to triatomic and polyatomic molecules (Simons, 1974; Simons and Novick, 1974; Carney, 1979; Diab and Simons, 1977). (Notice that, first, the Coulomb-subtracted Simons–Parr–Finlan expansion is of little interest, and second, there exist some papers in the literature in which the application of the SPF-expansion is incorrect and misleading [see Godawale *et al.* (1979, 1980), with a criticism by Tipping (1980)].

C. Thakkar Expansion Approach

Thakkar suggested a new independent variable $\xi_T(p; R) = \operatorname{sgn}(p)[1 - (R_e/R)^p]$, where p is a parameter which evidently is the generalization of $\xi_D(R)$ $(p = -1)$ and $\xi_{SPF}(R)$ $(p = 1)$. The Thakkar (T) expansion is obtained by replacing ξ_D with ξ_T in Eq. (1), where, accordingly, we have a_n^T instead of a_n^D (Thakkar, 1975). The first seven a_n^T are expressed in terms of a_n^D as follows (Thakkar, 1975):

$$
\begin{aligned}
a_0^D &= p^2 a_0^T \\
a_1^D &= p(\hat{a}_1^T - 1) - 1 \\
a_2^D &= (3/2)p(1 - \hat{a}_1^T) + p^2[-(3/2)\hat{a}_1^T + a_2^T + (7/12)] + (11/12) \\
a_3^D &= (7/4)p(\hat{a}_1^T - 1) + p^2[3\hat{a}_1^T - 2a_2^T - (7/6)] \\
&\quad + p^3[(5/4)\hat{a}_1^T - 2a_2^T + \hat{a}_3^T - (1/4)] - (5/6) \\
a_4^D &= (15/8)p(1 - \hat{a}_1^T) + p^2[-(17/4)\hat{a}_1^T + (17/6)a_2^T + (119/72)] \\
&\quad + p^3[-(25/8)\hat{a}_1^T + 5a_2^T - (5/2)\hat{a}_3^T + (5/8)] \\
&\quad + p^4[a_4^T - (3/4)\hat{a}_1^T + (13/6)a_2^T - (5/2)\hat{a}_3^T + (31/360)] + (137/180) \\
a_5^D &= -(29/15)p - (7/2)a_2^T p^2 - (25/3)a_2^T p^3 - (13/2)a_2^T p^4 - (5/3)a_2^T p^5 \\
&\quad + (25/6)\hat{a}_3^T p^3 + (15/2)\hat{a}_3^T p^4 + (10/3)\hat{a}_3^T p^5 - 3a_4^T p^4 - 3a_4^T p^5 \qquad (13) \\
&\quad + \hat{a}_5^T p^5 + (29/15)\hat{a}_1^T p + (21/4)\hat{a}_1^T p^2 + (125/24)\hat{a}_1^T p^3 + (9/4)\hat{a}_1^T p^4 \\
&\quad + (43/120)\hat{a}_1^T p^5 - (49/24)p^2 - (25/24)p^3 - (31/120)p^4 \\
&\quad - (1/40)p^5 - (7/10) \\
a_6^D &= (469/240)p + (967/240)a_2^T p^2 + (35/3)a_2^T p^3 + (299/24)a_2^T p^4 \\
&\quad + (35/6)a_2^T p^5 + (81/80)a_2^T p^6 - (35/6)\hat{a}_3^T p^3 - (115/8)\hat{a}_3^T p^4 \\
&\quad - (35/3)\hat{a}_3^T p^5 - (25/8)\hat{a}_3^T p^6 + (23/4)a_4^T p^4 + (21/2)a_4^T p^5 \\
&\quad + (19/4)a_4^T p^6 - (7/2)\hat{a}_5^T p^5 - (7/2)\hat{a}_5^T p^6 + a_6^T p^6 - (469/240)\hat{a}_1^T p \\
&\quad - (967/160)\hat{a}_1^T p^2 - (175/24)\hat{a}_1^T p^3 - (69/16)\hat{a}_1^T p^4 - (301/240)\hat{a}_1^T p^5 \\
&\quad - (23/160)\hat{a}_1^T p^6 + (6769/2880)p^2 + (35/24)p^3 + (713/1440)p^4 \\
&\quad + (7/80)p^5 + (127/20160)p^6 + (363/560)
\end{aligned}
$$

where $\hat{a}_k^T = \operatorname{sgn}(p)a_k^T$.

It is evident that p is a parameter which is chosen from the criterion of the best reproduction of a real diatomic potential energy function $U(R)$. There are some possibilities to choose from to satisfy this criterion. The first possibility is to choose p such that (Goble and Winn, 1979) $p = -(k_3R_3)/(3k_2) - 1 \equiv -a_1^{\mathrm{P}} - 1$. From Eqs. (9) and (10) it follows that

$$p = \alpha_e\omega_e/6B_e^2 \tag{14}$$

This choice of p provides the leading term in the T-expansion to reproduce both k_2 and k_3 exactly. In particular, we may choose the first correction parameter a_1^{T} to be zero. As a result we have the correct expression for p in a case when the real diatomic potential is just a Lennard–Jones type. Therefore, the T-expansion for that p is essentially an expansion in a series of Lennard–Jones potentials.

The parameter p has a clear physical meaning because $U(\xi_{\mathrm{T}})$ approaches the dissociation as a polynomial led by the term R^{-p}. This behavior has the promise that the T-series can approximate the anticipated long-range behavior of a weakly bonded species (Winn, 1981). Nevertheless, from Eq. (14) it follows that p is directly obtained from the equilibrium properties of a real $U(R)$.

In the case of an arbitrary p, one can introduce in addition branch cuts in the complex R-plane in order to ensure single-valued $U(\xi_{\mathrm{T}})$, because for $0 \leq R < +\infty$, $\xi_{\mathrm{T}}(p;\ \mathrm{R})$ can have more than one Riemann sheet. In particular, the following mappings result:

(a) $p > 0$

$$(0, \infty)_{\mathbf{R}} \xrightarrow{\xi_{\mathrm{T}}} (-\infty, 1)_{\xi_{\mathrm{T}}}$$

(b) $p < 0$

$$(0, \infty)_{\mathbf{R}} \xrightarrow{\xi_{\mathrm{T}}} (-1, \infty)_{\xi_{\mathrm{T}}}$$

In many cases [see, for example, Winn (1981)], the Thakkar power-series expansion has a nonphysical behavior at the repulsive wall; namely, for certain sets of parameters the repulsive wall disappears [we refer to the dashed-line curve in Fig. 3 of Winn (1981)].

Thakkar's coefficients have a very poor convergence property. In particular, for the T-coefficients obtained by Engelke (1978), we have ($p = 0.6886219$):

$$|a_1^{\mathrm{T}}/a_0^{\mathrm{T}}| = 0, \qquad |a_2^{\mathrm{T}}/a_1^{\mathrm{T}}| = \infty$$

$$|a_3^{\mathrm{T}}/a_2^{\mathrm{T}}| = 1.415019, \qquad |a_4^{\mathrm{T}}/a_3^{\mathrm{T}}| = 1.190095$$

Moreover, the nth-truncated Thakkar expansion has a maximum as an artifact in many cases (Winn, 1981; Goble *et al.*, 1977; Goble and Winn, 1981; Kryachko, 1983c). Such a maximum was also obtained by Engelke (1978) for $n = 4$ and $R \simeq 5R_e$. This model observation may be confirmed analytically. For example, if we truncate $dU(\xi_T(R))/dR$ at $\xi_T{}^3$, we have

$$\begin{aligned} dU(\xi_T)/dR = {} & (a_0^T p\xi_T/R)[2 + (3a_1^T - 2\,\mathrm{sgn}(p))\xi_T \\ & + (4a_2^T - 3a_1^T\,\mathrm{sgn}(p))\xi_T{}^2] \end{aligned}$$

Putting $dU(\xi_T)/dR = 0$, we obtain three roots ($a_1^T = 0$, $p > 0$):

$$\begin{aligned} R_1 &= R_e \\ R_{2,3} &= R_e[1 + (1/4|a_2^T|) \mp (1 + 8|a_2^T|)^{1/2}/(4|a_2^T|)]^{1/p} \end{aligned} \tag{15}$$

From Eq. (15) it follows that for certain values of a_2^T, at least one of $R_{2,3}$ lies on the real R-axis. Therefore, in our opinion, this is a direct corollary of such definition of p, Eq. (14). We suggest that this artifact may be removed by another manner of choosing p [see, for example, Kryachko (1983c)].

Therefore, from the detailed study of the Thakkar expansion carried out by Goble, Winn, and Engelke, we may conclude first that the nth-truncated T-series at $n = 2$ gives the adequate description of $U(R)$ in the region $R \gtrsim R_e$. The same result is true for the SPF-series. However, for $n = 1$, the T-series is superior to the D- and SPF-series. Second, for $p < 0$, the radius of convergence is at most the interval $0 < R < 2^{1/|p|}R_e$. And finally, the T-approach overestimates the dissociation energies for Mg_2 and Ca_2 and fails to recover the correct long-range behavior. For both molecules, the T-series reproduces poorly the Rydberg–Klein–Rees potentials (see Section XI).

D. Ogilvie–Tipping Method

Following the suggestion by Tipping (1974), Ogilvie, in 1974, proposed their (OT) new independent variable $\xi_{OT}(R) = (R - R_e)/(R + R_e)$ to obtain a new form of a power-series expansion $U(\xi_{OT}(R))$ (the replacing procedure is same as in the preceding sections) (Ogilvie, 1974, 1976). ξ_{OT} ranges the interval $[-1, 1]$, and $\xi_{OT}(R)$ is an analytical function in the whole complex R-plane except for the point $R = -R_e$. It is important to note that $\xi_{OT}(R)$ is regular at $R = 0$. This fact makes it possible to describe adequately $U(R)$ near the origin $R = 0$. Moreover, the truncated OT-series yields finite values of $U(\xi_{OT}(R))$ at both $R = 0$ and $R = \infty$, which are absent in the preceding power-series expansions.

Without any difficulty, one can obtain the relations between the D- and OT-coefficients. In particular, for the first five coefficients we have

(Engelke, 1978)

$$
\begin{aligned}
a_0^{\mathrm{OT}} &= 4a_0^{\mathrm{D}} \\
a_1^{\mathrm{OT}} &= 2(1 + a_1^{\mathrm{D}}) \\
a_2^{\mathrm{OT}} &= 4a_2^{\mathrm{D}} + 6a_1^{\mathrm{D}} + 3 \\
a_3^{\mathrm{OT}} &= 4(2a_3^{\mathrm{D}} + 4a_2^{\mathrm{D}} + 3a_1^{\mathrm{D}} + 1) \\
a_4^{\mathrm{OT}} &= 16a_4^{\mathrm{D}} + 40a_3^{\mathrm{D}} + 40a_2^{\mathrm{D}} + 20a_1^{\mathrm{D}} + 5
\end{aligned}
\qquad (16)
$$

Engelke carried out a detailed analysis of the OT-expansion (Engelke, 1978). He showed that when a_0^{D} through a_2^{D} are known, the T- and SPF-series are slightly superior to the OT-series for $R > R_e$. Also, he proved that in this case the OT-series has no spurious maxima, as does the T-series, at least for $R \leq 7.5R_e$. (The T-series artifact arises at $R \simeq 3.7R_e$, when a_0^{D}, a_1^{D}, a_2^{D}, a_3^{D}, and a_4^{D} are known.) In the region $R < R_e$ the picture is vice versa. The same conclusions are also true for the CSOT-expansion. Engelke summarized that the CSOT-series is the best series representation for $0 \leq R \leq 5R_e$ for the case in which a_0^{D}, a_1^{D}, and a_2^{D} are known.

E. Generalized Power-Series Expansion

As we have shown in the preceding discussions, all the independent variables, except for Thakkar's definition, are related by the formula

$$\xi(\mu\nu\sigma|R) \equiv [(R - R_e) + \sigma R_e]/[\mu R_e + \nu(R - R_e)] \qquad (17)$$

where in particular we have

$$
\begin{aligned}
\xi(\mu = 1, \nu = 0, \sigma = 0|R) &\equiv \xi_{\mathrm{D}}(R) \\
\xi(\mu = \nu = 1, \sigma = 0|R) &\equiv \xi_{\mathrm{SPF}}(R) \\
\xi(\mu = 2, \nu = 1, \sigma = 0|R) &\equiv \xi_{\mathrm{OT}}(R)
\end{aligned}
\qquad (18)
$$

Then, in these notations, the Thakkar variable has the form

$$\xi_{\mathrm{T}}(R) \equiv \mathrm{sgn}(p)[1 - \xi^{-p}(\mu = 1, \nu = 0, \sigma = 1|R)]$$

Therefore, Eq. (17) is the so-called homomorphic transformation

$$R \xrightarrow{\xi} \xi(\mu\nu\sigma|R) \qquad (19)$$

with the condition $\xi(\mu\nu\sigma|R_e) = 0$. From Eq. (18) it follows that all known independent variables do not cover all ranges of parameters μ and ν. In our opinion, there is a field of study, first of all, to correlate values of these parameters with more adequate representation of a real diatomic curve. Then ξ ranges the interval $[-1/(\mu - \nu), 1/\nu]$ when R lies in the interval $[0, \infty)$ for $\sigma = 0$. For known sets of parameters, Eqs. (18) and (19), we have the following diagram:

$$\begin{tikzcd}
 & & {[-1, 1]} & \\
{[0, \infty)_{\mathbf{R}}} \arrow[urr, "\mathrm{OT}"] \arrow[dr, "\mathrm{T}"'] & & {[-1, \infty)} \arrow[r, "\mathrm{D}"] & {[-1, \infty)} \\
 & {} \arrow[ur, "p<0"] \arrow[r, "p>0"'] & {(-\infty, 1]} \arrow[r, "\mathrm{SPF}"'] & {(-\infty, 1]}
\end{tikzcd}$$

In 1979, Engelke examined the fine structure of this diagram. He proposed the generalized independent variable

$$\xi_{\mathrm{E}}(p|R) \equiv \operatorname{sgn}(p)[1 - \xi^{-p}(\mu, \nu = 0, \mu)] \tag{20}$$

where p and μ are parameters. [For $\mu = p/\gamma - 1$ with $\gamma > 0$, $\xi_{\mathrm{E}}(p|R)$ was independently suggested by Mattera *et al.* (1980).]

The Engelke (E) power-series expansion is obtained from Eq. (1) via replacing $\xi_{\mathrm{D}}(R)$ by $\xi_{\mathrm{E}}(p|R)$. It is evident that the Engelke parameterization involves as special cases all known power-series expansions. The transformation, Eq. (20), maps the positive real R-axis onto the interval

$$([1 - (1 + \mu^{-1})^{p}], 1) \qquad \text{for} \quad \mu > 0 \qquad \text{and} \qquad p > 0$$

$$([(\mu/(\mu + 1))^{|p|} - 1], \infty) \qquad \text{for} \quad \mu > 0 \qquad \text{and} \qquad p < 0$$

In the case of $p > 0$ and $\mu > 0$, the E-variable has no singularities for all R between $(0, \infty)$. Engelke derived the following relations for the first five E-coefficients (Engelke, 1979):

$$\begin{aligned}
a_0^{\mathrm{E}} &= p^{-2}(1 + \mu)^2 a_0^{\mathrm{D}} \\
a_1^{\mathrm{E}} &= p^{-1} \operatorname{sgn}(p)[(1 + \mu)a_1^{\mathrm{D}} + (1 + p)] \\
a_2^{\mathrm{E}} &= p^{-2}[(1 + \mu)^2 a_2^{\mathrm{D}} + (3/2)p(1 + p)\hat{a}_1^{\mathrm{E}} - (1/12)(1 + p)(7p + 11)] \\
a_3^{\mathrm{E}} &= p^{-3} \operatorname{sgn}(p)[(1 + \mu)^3 a_3^{\mathrm{D}} + 2p^2(1 + p)a_2^{\mathrm{E}} \\
&\quad - (1/4)p(p + 1)(7 + 5p)\hat{a}_1^{\mathrm{E}} + (1/12)(p + 1)(p + 2)(3p + 5)] \\
a_4^{\mathrm{E}} &= p^{-4}[(1 + \mu)^4 a_4^{\mathrm{D}} + (5/2)p^3(p + 1)\hat{a}_3^{\mathrm{E}} - (1/6)p^2(p + 1)(13p + 7)a_2^{\mathrm{E}} \\
&\quad + (p/2)(p + 1)\{(p + 1)(p + 2) + (1/4)(p + 1)^2 + (1/4)(p + 2) \\
&\quad \times (p + 3)\}a_1^{\mathrm{E}} - (1/12)(p + 1)(p + 2)\{(1/6)(p + 1)(5p + 13) \\
&\quad + (1/5)(p + 3)(p + 4)\}]
\end{aligned} \tag{21}$$

where $\hat{a}_k^{\mathrm{E}} = \operatorname{sgn}(p)a_k^{\mathrm{E}}$.

Therefore, we may expect that the great flexibility of Engelke's approach would permit us to obtain an improved power-series representation of a real diatomic potential. The properties of such a representation for various μ and p are examined in detail by Engelke (1979). The only question we would like to mention concerns the problem of the choice of p and μ. The first and obviously the best, in our opinion, way consists in the consideration of p and μ as variational parameters to improve the quality of the power-series representation. The second way, as pointed out by Engelke, is the way of choosing p to describe correctly the real long-range behavior. Here we need to take p as being equal to the power of the leading term in the multipole long-range expansion. The third way, developed also by Engelke, is to force higher terms in $U(\xi_e(p|R))$ to be zero by using the (p, μ)-flexibility. These approaches have not yet been solved completely.

Finally, following Engelke, we give some comments concerning all the power-series representations discussed so far. All the independent variables are chosen in such a manner that they become zero in the equilibrium. But this requirement is not general and fundamental; at least, nobody has proved this to be the case. Simply, it is a very convenient way to describe adequately a real diatomic curve. At the same time we may choose any other variable, for example, the scaled distance $\xi = R/R_e$, and propose some versions of an expansion via ξ [see, for instance, the expansion suggested by Engelke (1979)].

All of these representations are based on the Taylor series of $U(\xi(R))$ in the neighborhood of $R = R_e$ via powers of the chosen variable $\xi = \xi(R)$. The only problem is to choose a convenient variable-function $\xi = \xi(R)$. Let us assume that we find this $\xi(R)$, and that it works adequately, but at the same time the problem of convergence will arise (Beckel and Engelke, 1968; Beckel, 1976). And finally we must truncate the expansion, and this truncation may result in artifacts, i.e., we have some very difficult problems which are the corollaries of the adopted Taylor expansion.

III. Short-Range Behavior of Diatomic Interactions

The quantum-chemical study of diatomic interactions can be classified into three parts based on the range of the internuclear separation R. They are as follows: (1) small R—$R \sim 0$; (2) intermediate R—$R \sim R_e$; (3) large R—$R \rightarrow \infty$. The long-range behavior of diatomic interactions is well known: any quantum chemist writes quickly the necessary formulas that are derived from the perturbation approach suggested first by London and developed by many workers [see, for example, Margenau and Kestner (1971), Hirschfelder *et al.* (1964b), Kaplan (1982), Buckingham (1978), Claverie (1978), and Ahlrichs (1976)]. This is a well-known $1/R$ series expansion of the interaction potential [see Eq. (I.7)]. With the other two regions, the matter is more complex. The analytical representation of diatomic interactions via power-series expansion has been examined in detail in Section II.

In this section, we are concerned only with the short-range behavior of diatomic interactions. This problem was studied extensively by many workers (Morse and Stueckelberg, 1929; Bethe, 1933; Baber and Hassé, 1935; Coulson and Duncanson, 1938; Matsen, 1953; Huzinaga, 1956, 1957; Buckingham, 1958; Bingel, 1957, 1959, 1960, 1962, 1963a,b; Levine, 1964; Byers-Brown and Steiner, 1966; Byers-Brown and Power, 1970; Byers-Brown, 1966; Claverie, 1970). The main goal of these studies consists in the exploration of a perturbation scheme for the electronic energy of a given diatomic molecule:

$$W(R; Z_A, Z_B) = U(R) - Z_A Z_B / R \tag{1}$$

It was suggested by the united-atom approach for $W(R)$ that

$$\begin{aligned} W(R; Z_A, Z_B) = {} & W_0(Z_A, Z_B) + R^2 W_2(Z_A, Z_B) + R^3 W_3(Z_A, Z_B) \\ & + R^4 W_4(Z_A, Z_B) + \cdots \end{aligned} \tag{2}$$

with $W_1 = 0$. Notice that this expansion, Eq. (2), is the Taylor series at $R = 0$. Therefore, it directly follows the limiting description of $W(R)$ for small R. The evolution of developments of the united-atom idea is illustrated in Table I. Notice that this evolution was not smooth enough—there exist some critical catastrophical periods, and this field is not yet developed completely.

Let us consider the united-atom expansion, Eq. (2). The leading term W_0 is the energy of the united atom with a nuclear charge $Z_{ua} = Z_A + Z_B$, and it is natural that for a one-electron united atom

$$W_0(Z_A, Z_B) = -(1/2) Z_{ua}^2 \tag{3}$$

Before deriving the analytical expressions for W_i, we would like to point out some interesting properties of $W(R; Z_A, Z_B)$ which were discussed by Byers-Brown and Power (1970), and for one-electron systems, by Byers-Brown and Steiner (1966). They are as follows:

(a) $W(R; Z_A, Z_B) = W(R; Z_B, Z_A)$, (4a)

(b) only for one-electron diatomics

$$W(R; Z_A, Z_B) = Z_{ua}^2 \mathscr{W}(R Z_{ua}, Z_A Z_B / Z_{ua}^2) \tag{4b}$$

The latter formula, Eq. (4b), expresses the second-order homogeneity property of W with respect to Z_A, Z_B, and R. For simplicity, we consider only one-electronic diatomic molecules. In this particular case, we have (Byers-Brown and Steiner, 1966)

$$W_0 = -(1/2) Z_{ua}^2 \tag{5a}$$

$$W_2 = (2/3) Z_A Z_B Z_{ua}^2 \tag{5b}$$

TABLE I

EVOLUTION OF THE UNITED-ATOM IDEAS

Authors	Essence of their work
Morse and Stueckelberg (1929)	First-order approach; application to the lowest states of H_2^+
Bethe (1933)	Analytical expression for W in a particular case of an arbitrary state of H_2^+
Baber and Hassé (1935)	Generalization of W_2
Coulson and Duncanson (1938)	First-order approach; application to HeH^{2+} based on Li^{2+} united atom
Matsen (1953)	Extension of Morse and Stueckelberg (1929) for H_2^+
Huzinaga (1956, 1957)	Single-center calculations on H_2^+ and H_2; He–He diatomic interactions
Buckingham (1958)	$W_1 = 0$; first-order approach for many-electron diatomics
Bingel (1957, 1959, 1960, 1962, 1963a,b)	General approach $W_2 = Z_A Z_B/(Z_A + Z_B) \times [(\frac{2}{3})\pi\rho_{ua}(0) - (\frac{1}{2}) \int P_2(\cos\theta) r^{-3} \rho_{ua}(\mathbf{r})\, d\mathbf{r}]$ where $\rho_{ua}(\mathbf{r})$ is the electron density of the united atom; the second term vanishes for the S-state when $\rho_{ua}(0) = Z_{ua}^3/\pi$
Levine (1964)	Criticism of some statements by Bingel; the derivation of the second-order energy formula for a homonuclear one-electron diatomic up to the R^3 order

$$W_3 = -(2/3) Z_A Z_B Z_{ua}^3 \tag{5c}$$

$$W_4 = (2/5) Z_A Z_B [1 - (64/27)(Z_A Z_B / Z_{ua}^2)] Z_{ua}^4 \tag{5d}$$

$$W_5 = -(8/45) Z_A Z_B [5(Z_A Z_B/Z_{ua}^2) \log(2\gamma R Z_{ua}) + 1 - (199/12)(Z_A Z_B/Z_{ua}^2)] Z_{ua}^5 \tag{5e}$$

where γ is the Euler constant.

In particular, for the H–H$^+$ interaction, with the united atom being He$^+$ with $Z_{ua} = 2$, Eqs. (5a)–(5e) result in

$$W_0 = -2 \tag{6a}$$

$$W_2 = 8/3 \tag{6b}$$

$$W_3 = -16/3 \tag{6c}$$

$$W_4 = 352/135 \tag{6d}$$

$$W_5 = 32[151/270 - (2/9) \log(4\gamma R)] \tag{6e}$$

These terms are represented in Fig. 2. It follows that the range of validity of the corresponding nth-truncated expansion, Eq. (2), is about 0.1, 0.2, and $0.3a_0$ for $n = 2, 3$, and 5, respectively, where a_0 is the Bohr radius. Notice that there exists a discrepancy between the formulas obtained by Bingel (see Table I) and Eqs. (5a)–(5e). The last equation, Eq. (5e), involves $R^5 \log R$, which emphasizes the R-dependence of W_5 and the corresponding nonanalyticity of $W(R)$ at $R = 0$. Byers-Brown and Steiner (1966) suggested that the logarithmic dependence originates from the Coulomb singularity at $R = 0$.

Figure 2 gives a very small range of validity of the united-atom expansion even including the logarithmic term. To avoid this problem, Byers-Brown and Power (1970) proposed new formulas to describe the short-range behavior of diatomic interactions. [This approach was first outlined by Byers-Brown (1966).] In our particular case of the H–H$^+$ interaction, they derived (Byers-Brown and Power, 1970)

$$W^{[1]}(R) = 1 - 1/2R + (1 + 1/2R)\exp(-2R) \tag{7}$$

which is also depicted in Fig. 2. It is shown that this term, $W^{[1]}(R)$, gives a very good approximation to the real curve up to $R = 1$. Therefore, the

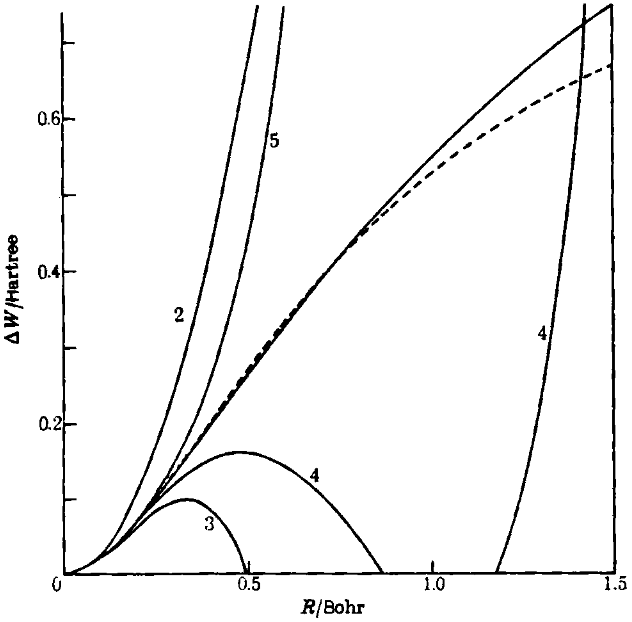


Fig. 2. The short-range behavior of the H–H$^+$ interaction; (——), exact; (---), Eq. (7); 2, R^2W_2, Eq. (6b); 3, $R^2W_2 + R^3W_3$, Eqs. (6b) and (6c); 4, $R^2W_2 + R^3W_3 + R^4W_4$, Eqs. (6b)–(6d); 5, terms up to R^5W_5, Eqs. (6b)–(6e). (Reproduced from Byers-Brown and Power, 1970.)

new perturbation scheme by Byers-Brown and Power (1970) and, in particular, its first-order approach adequately describe the short-range behavior of diatomic interactions and provide a basis for constructing more realistic model diatomic potentials, when based on the united-atom approach. Recently, Claverie suggested the diatomic potential describing a short-range behavior of the He–He interaction in the following form (Claverie, 1970):

$$U(R) = 4S^2/R + (\zeta - 1.375)\zeta R - (1/2)\log(\zeta R) + (1/2)(11 - 6\zeta - \gamma) \tag{8}$$

where

$$S(R) = [1 + \zeta R + (\zeta R)^2/3] \exp(-\zeta R)$$

is the overlap integral, and ζ is the exponent of the 1s atomic orbital.

IV. Schrödinger Equation Picture

In the preceding sections we have discussed mainly the behavior of diatomic interactions and reliable analytical representations. In the present section we connect these ideas with spectra of diatomic molecules. To advance this aspect, we need to solve the Schrödinger equation with the corresponding model diatomic potential energy function. It is evident that in general this problem is beyond our strength. Anybody remembers from the elementary quantum-mechanical course that we can obtain the exact Schrödinger equation solution only for some particular cases, which, from the viewpoint of diatomic potential theory, are essentially trivial and are not of interest. Then what can we do? In the literature there exist some mathematical approaches based on physical grounds (of semiclassical or quantum-mechanical nature) to obtain approximately energy eigenfunctions and eigenvalues of diatomics from the first principles, i.e., from a given analytical representation of diatomic interactions, to which the discussions in this section are devoted.

A. Vibrational–Rotational Energy Formulas

In the literature it is seen that some approximate formulas for energy eigenvalues $E(v, J)$ for diatomics have been obtained. In fact, this is the traditional approach for chemists and physicists who study vibrations of molecules only in the lowest few vibrational energy states. For such vibrations the diatomic potential is well approximated by the harmonic oscillator with "smaller" anharmonic corrections, i.e., the Dunham (D) expression (see Section II,A) serves as a good approximation for that study (Herman *et al.*, 1970; Stwalley, 1978). The only point to note is that the validity and therefore the utility of the D-formula for $E(v, J)$ [Eq. (II.7)] decline as v increases.

Evidently, it is desirable from this traditional point of view to describe in an analytical manner the energy eigenvalues for vibrational levels near the dissociation limit. This problem is of great importance. In recent years there has been great progress in solving this problem (Stwalley, 1970, 1973c, 1978; Stwalley and Zemke, 1976; Stwalley *et al.*, 1978; Le Roy, 1972, 1973; Le Roy and Bernstein, 1970, 1971; Goscinski, 1972; Goscinski and Tapia, 1972; Yee, 1974; Le Roy and Barwell, 1975; Barwell, 1975; Diskinson and Bernstein, 1970) and in studying diatomic properties in this region. It is evident that properties are in strong correlation with the diatomic potential long-range behavior, or, correctly speaking, with the neighborhood of the outer turning points of the level. Physically, this may be explained in that when the molecule repeatedly vibrates classically from an inner turning point (~1 Å) to an outer turning point (~10–100 Å), it spends almost all of its lifetime on the potential tail (Stwalley *et al.*, 1978).

Therefore, to study rotationless levels ($J = 0$), spacing near the dissociation limit, one needs to represent analytically and sufficiently well this tail. Le Roy and Bernstein (1970) and Stwalley (1970) suggested the following form:

$$U(R) = D_e - C_{n_0}/R^{n_0}, \qquad n_0 > 2 \tag{1}$$

i.e., they assumed the dominant role of the first two terms in the dispersion series of $U(R)$ [Eq. (I.7)]. Substituting this formula, Eq. (1), into the semiclassical phase integral, one can obtain the vibrational energy eigenvalues (Le Roy and Bernstein, 1970, 1971; Stwalley, 1970):

$$E(v, J = 0) = D_e - X_{n_0}(0)(v_D - v)^{2n_0/(n_0-2)} \tag{2}$$

where $X_{n_0}(0)$ is a constant and v_D is a vibrational quantum number in the dissociation limit. In general, v_D is noninteger. The utility of Eq. (2) is constrained by the correctness of Eq. (1).

In the framework of this approximation, Le Roy and co-workers (Le Roy, 1972, 1973; Le Roy and Barwell, 1975; Barwell, 1975) and Stwalley (1973c) obtained the expressions for the rotational constant B_v and higher order rotational constants:

$$B_v = X_{n_0}(1)(v_D - v)^{4/(n_0-2)} \tag{3a}$$

$$D_v = -X_{n_0}(2)(v_D - v)^{-(2n_0-8)/(n_0-2)} \tag{3b}$$

$$H_v = X_{n_0}(3)(v_D - v)^{-(4n_0-12)/(n_0-2)} \tag{4a}$$

$$L_v = X_{n_0}(4)(v_D - v)^{-(6n_0-16)/(n_0-2)} \tag{4b}$$

where

$$X_{n_0}(k) = [\mu^{n_0}(C_{n_0})^2]^{-1/(n_0-2)}\bar{X}_{n_0}(k) \tag{5}$$

and $\bar{X}_{n_0}(k)$ are numerical factors expressed in terms of the familiar gamma function (Stwalley, 1973c) and μ is the reduced mass.

In particular, for $n_0 = 4$ and 6 we have, respectively [see Eq. (I.12)],

$$E^{n_0=4}(v, J) = E^{n_0=4}(v, J = 0) + \sum_{k=1}^{N} X_4(k)(v_D - v)^{4-2k}[J(J + 1)]^k \tag{6}$$

$$E^{n_0=6}(v, J) = E^{n_0=6}(v, J = 0) + \sum_{k=1}^{N} X_6(k)(v_D - v)^{3-2k}[J(J + 1)]^k \tag{7}$$

However, the reader may ask how to obtain v_D? This unknown parameter can be obtained via the procedure proposed by Le Roy and Barwell (1975). However, the validity of that procedure has a problem, at least, for two reasons. The first concerns the truncation of $J(J + 1)$ series, because this truncation requires the estimation of the omitted terms, which is argued by Diskinson and Bernstein (1970). These authors have shown that the highest unpredissociated rotational level for a given v corresponds to the following value of $J(J + 1)$:

$$[J(J + 1)]_v^{\ddagger} = [2\pi^2/(6 - 3\sqrt{3})](v_D - v)^2 \tag{8}$$

The second reason consists in the validity of Eqs. (1) and (2), because its derivation is based on the assumption that the tail of a given diatomic potential near the outer turning point of the level is approximated by the first two terms. In general, this assumption may not be correct and one can include higher order terms (Goscinski, 1972; Goscinski and Tapia, 1972). The breaking of this assumption requires more detailed study (Le Roy, 1972, 1973; Barwell, 1975).

Thus, we have two expressions for $E(v, J)$, Eqs. (II.7) and (2), as functions of v and J. The first, the Dunham expression, is valid for v near the bottom of the potential well. The second, the Le Roy–Bernstein–Stwalley expression, is applicable in the dissociation limit. Naturally, it would be expected to derive a formula for $E(v, J)$ in the complete space, whose limiting cases coincide with Eqs. (II.7) and (2). Evidently, this formula, if it exists in general, may have a more complex expression. One of the possible ways to construct this formula is based on the application of the Padé approximant technique. This way was exploited by Beckel and co-workers (Hashemi-Attar *et al.*, 1979; Hashemi-Attar and Beckel, 1979), who suggested

$$E(v, J = 0) = D_e - (v_D - v)^m[L/N](v) \tag{9}$$

where (for details see Section V)

$$[L/N](v) = \sum_{i=0}^{L} p_i(v_\mathrm{D} - v)^i / [1 + \sum_{j=1}^{N} q_j(v_\mathrm{D} - v)^j] \tag{10}$$

In Eq. (10), $\{p_i\}_{i=0}^{L}$ and $\{q_j\}_{j=1}^{N}$ are the sets of parameters. In the limit of $v \rightarrow v_\mathrm{D}$, one can obtain easily

$$E(v) = D_\mathrm{e} - p_0(v_\mathrm{D} - v)^m \tag{11}$$

which coincides with Eq. (2) if $p_0 = X_{n_0}(0)$ and $m = 2n_0/(n_0 - 2)$.

In the lower limit of $v \rightarrow 0$, Eq. (9) transforms to the corresponding Dunham expression, and we obtain

$$\begin{aligned}
Y_{00} &= D_\mathrm{e} - (v_\mathrm{D} + \tfrac{1}{2})^m Q^{-1} \sum_{i=0}^{L} p_i(v_\mathrm{D} + \tfrac{1}{2})^i \\
Y_{10} &= (v_\mathrm{D} + \tfrac{1}{2})^m Q^{-1} \left[\sum_{i=1}^{L} i p_i(v_\mathrm{D} + \tfrac{1}{2})^{i-1} + \left(\sum_{i=0}^{L} p_i(v_\mathrm{D} + \tfrac{1}{2})^i\right)\right. \\
&\quad \times \left.\left(\sum_{j=1}^{N} j q_j(v_\mathrm{D} + \tfrac{1}{2})^{j-1}\right)\right] + mQ^{-1} \sum_{i=0}^{L} p_i(v_\mathrm{D} + \tfrac{1}{2})^i(v_\mathrm{D} + \tfrac{1}{2})^{m-1} \\
Y_{20} &= -\tbinom{m}{2}(v_\mathrm{D} + \tfrac{1}{2})^{m-2}Q^{-1}I_0 - m(v_\mathrm{D} + \tfrac{1}{2})^{m-1}Q^{-1}I_1 - (v_\mathrm{D} + \tfrac{1}{2})^m Q^{-1}I_2 \\
Y_{30} &= \tbinom{m}{3}(v_\mathrm{D} + \tfrac{1}{2})^{m-3}Q^{-1}I_0 + \tbinom{m}{2}(v_\mathrm{D} + \tfrac{1}{2})^{m-2}Q^{-1}I_1 \\
&\quad + mQ^{-1}(v_\mathrm{D} + \tfrac{1}{2})^{m-1}I_2 + (v_\mathrm{D} + \tfrac{1}{2})^m Q^{-1}I_3, \qquad \text{etc.}
\end{aligned} \tag{12}$$

where

$$\begin{aligned}
I_0 &= \sum_{i=0}^{L} p_i(v_\mathrm{D} + \tfrac{1}{2})^i \equiv I \\
J &= \sum_{j=1}^{N} q_j(v_\mathrm{D} + \tfrac{1}{2})^j \\
Q &= 1 + J \\
I_1 &= dI/dv_\mathrm{D} + Q^{-1}I[dJ/dv_\mathrm{D}] \\
I_2 &= Q^{-2}I[dJ/dv_\mathrm{D}]^2 + Q^{-1}[dI/dv_\mathrm{D}][\mathrm{d}J/dv_\mathrm{D}] \\
&\quad + [d^2I/dv_\mathrm{D}^2] + Q^{-1}I[d^2J/dv_\mathrm{D}^2] \\
I_3 &= I(Q^{-3}[dJ/dv_\mathrm{D}] + 2Q^{-2}[dJ/dv_\mathrm{D}][d^2Jdv_\mathrm{D}^2] + Q^{-1}[d^3J/dv_\mathrm{D}^3]) \\
&\quad + Q^{-1}[dI/dv_\mathrm{D}](Q^{-1}[dJ/dv_\mathrm{D}] + [d^2Jdv_\mathrm{D}^2]) \\
&\quad + Q^{-1}[d^2I/dv_\mathrm{D}^2][dJ/dv_\mathrm{D}] + [d^3Idv_\mathrm{D}^3]
\end{aligned} \tag{13}$$

and so on.

Therefore, the parameters $\{p_i\}_{i=0}^{L}$ and $\{q_j\}_{j=1}^{N}$ are not independent but are related via Eqs. (12). Beckel and co-workers (Hashemi-Attar *et al.*, 1979) determined these sets of parameters from Y_{i0}, C_{n0}, and n_0 using the fitting procedure directed from the energy level data. They applied the nonlinear minimization technique to effect a least-squares fit of the first energy differences $\Delta E_c(v + \frac{1}{2})$ calculated from Eq. (11) to the accurate first differences $\Delta E_a(v + \frac{1}{2})$. In other words, they minimized the quantity

$$F = \sum_{v=0} [\Delta E_c(v + \tfrac{1}{2}) - \Delta E_a(v + \tfrac{1}{2})]^2 \tag{14}$$

where the ΔE_a are the vibrational energy differences obtained for the ground-state $H_2{}^+$ and H_2 diatomic potentials (Beckel *et al.*, 1970). For the details of this procedure, we refer to papers by Hashemi-Attar *et al.* (1979), Le Roy and Carley (1980), and Carney *et al.* (1978). The only problem arising here is that the multiparameter minimization is a very difficult problem: on the hypersurface of parameters there will be a large number of local minima and it is a problem to determine the global minimum, and it is also difficult to be certain whether the global minimum for F is found. That procedure has a very strong dependence on the choice of the initial set of parameters; to decrease the risk in omitting the global minimum, Hashemi-Attar *et al.* (1979) started the minimization procedure from a large number of initial sets. For example, in a particular case of $H_2{}^+$, their best results were registered in Fit No. 20 (Table II), for which the root mean square error for ΔE_c is 0.006 cm^{-1} and the maximum error

TABLE II

CHARACTERISTICS OF EQ. (IV.12) FITS WITH MISSING TERMS[a]

$[L/N](v)$ approximation [Eq. (IV.10)]	Root mean square errors in ΔE_c (cm^{-1}) [see Eq. (IV.14)]	Maximum error for any ΔE_c (cm^{-1})	v_D	m
$[4/2]_{p3}$	0.12	0.30	19.23	4.11
$[4/2]_{p1,p2}$	0.25	0.69	19.11	3.81
$[4/2]_{p1,p2,p3}$	0.38	0.58	19.16	3.85
$[2/2]_{q1}$	0.46	0.87	19.32	4.14
$[2/3]_{q1}$	0.08	0.17	19.37	4.66
$[2/3]_{q1,q2}$	1.99	3.99	20.08	5.47
$[2/4]_{q3}$	0.006	0.013	19.76	6.08
$[2/4]_{q1,q2}$	1.57	2.97	20.08	5.81
$[2/4]_{q1,q2,q3}$	3.71	8.57	21.14	6.85

[a] The missing terms are indicated by coefficients as subscripts. Application to the $H_2{}^+$ ground state. Fit No. 20 is underlined (Hashemi-Attar *et al.*, 1979).

TABLE III

COMPARISON OF THEORETICAL FIRST VIBRATIONAL ENERGY DIFFERENCES $\Delta E(v + \frac{1}{2})$ FROM EQ. (IV.12) WITH EXPERIMENTAL VALUES[a]

$v + \frac{1}{2}$	Theoretical $[L/N] = [1/3]$	 $[L/N] = [0/4]$	Experimental [Herzberg and Howe (1959)]
$\frac{1}{2}$	4161.20	4161.20	4161.14
$1\frac{1}{2}$	3925.83	3925.83	3925.98
$2\frac{1}{2}$	3695.37	3695.36	3695.24
$3\frac{1}{2}$	3467.95	3467.95	3468.01
$4\frac{1}{2}$	3241.55	3241.55	3241.56
$5\frac{1}{2}$	3013.84	3013.85	3013.73
$6\frac{1}{2}$	2782.12	2782.13	2782.18
$7\frac{1}{2}$	2543.15	2543.15	2543.14
$8\frac{1}{2}$	2292.90	2292.90	2292.96
$9\frac{1}{2}$	2026.29	2026.27	2026.26
$10\frac{1}{2}$	1736.64	1736.63	1736.66
$11\frac{1}{2}$	1415.04	1415.04	1414.98
$12\frac{1}{2}$	1049.14	1049.17	1049.18
$13\frac{1}{2}$	621.97	621.95	621.96
$D - E_{v=14}$	144.7	145.0	145.0[b]

[a] Values in cm^{-1}. Application to the H_2 ground state (Hashemi-Attar and Beckel, 1979).

[b] Assumption: $D_0 = 36118.0\ \mathrm{cm}^{-1}$.

is $0.013\ \mathrm{cm}^{-1}$. At the same time, Fit No. 20 predicts $D_e - E_{19}$ equal to $0.21\ \mathrm{cm}^{-1}$, but the correct value is $0.70\ \mathrm{cm}^{-1}$. The error of $0.49\ \mathrm{cm}^{-1}$ is moderate in an absolute sense, but in a relative sense it is about 70% of the correct value of $D_e - E_{19}$. Therefore, this minimization procedure needs further improvements. Nevertheless, the step done by Beckel and co-workers (Hashemi-Attar *et al.*, 1979; Hashemi-Attar and Beckel, 1979) is of great importance in the analytical description of vibrational energy levels of diatomics, and awaits a large variety of applications.

Finally, we would like to summarize. The vibrational formula suggested by Beckel and co-workers (Hashemi-Attar *et al.*, 1979; Hashemi-Attar and Beckel, 1979) is very useful and one can apply it to represent accurately energy differences between adjacent vibrational levels in the Born–Oppenheimer approach. To emphasize strongly this statement, we refer the reader to Table III. Equation (9) describes accurately the vibrational energy level spacing for diatomics. However, we must apply the nonlinear minimization to the F-fitting procedure. In the authors' opinion, in the framework of that approach, the Padé approximant $[L/N](v)$ constructed from the best developed traditional Padé technique may be useful, since it is free from the choice of initial sets and it provides the unique result (see also Section V).

B. WKBJ Approach

This approach is named after its founders—Wentzel (1926), Kramers (1926), Brillouin (1926a,b), and Jeffreys (1925). The WKBJ method is one of the powerful approximate approaches of quantum mechanics. Although in the present discussion we are concerned only with its application to obtaining approximate eigenvalues for bound states of the one-dimensional Schrödinger equation, such application does not cover all of its range and its force.

Dunham (1932) was the first who understood the ideas and force of this method, and applied the WKBJ approach to the derivation of the second and third nonzero energy terms of the one-dimensional Schrödinger equation with the D-version of an anharmonic potential (see also Krieger *et al.*, 1967). Afterward and up to recent times, so many authors have applied the WKBJ method that if we attempt to enumerate them all, then quite half of the present article would be represented by the references alone. For the inquisitive reader we refer to some papers (Krieger *et al.*, 1967; Kesarwani and Varshni, 1978, 1980; Zwaan, 1929; Kirschner and Watson, 1973; Stettler and Shatas, 1971; Fröman and Fröman, 1965; Killingbeck, 1980; Hecht and Mayer, 1957) in which, without any difficulties, a whole body of literature devoted to the problem may be found; i.e., by the principle of the Russian popular tale, which in our version becomes "a reference, by reference, by reference, etc., . . . ," the reader will "extract a turnip," i.e., a key to the essence.

While the reader may find recurrently that key, we present the basic idea of the WKBJ method, which consists in inserting into the one-dimensional Schrödinger equation

$$d^2\Psi(R)/dR^2 + (2\mu/\hbar^2)[E - U(R)]\Psi(R) = 0 \tag{15}$$

the wave function $\Delta(R)$ of the definite form of

$$\Psi(R) = \exp[(i/\hbar) \int \Phi(R)\, dR] \tag{16}$$

where $\Phi(R)$ is expanded in the powers of $\hbar$:

$$\Phi(R) = \sum_{k=0}^{\infty} (\hbar/i)^k \Phi_k(R) \tag{17}$$

Further equating the coefficients of successive powers of $\hbar$ to zero, one can determine Φ_k recurrently (Kesarwani and Varshni, 1980):

$$\Phi_0 = \pm[2\mu(E - U)]^{1/2} \tag{18a}$$

$$d\Phi_{k-1}/dR = -\sum_{m=0}^{k} \Phi_{k-m}\Phi_m, \qquad k = 1, 2, \ldots \tag{18b}$$

Solving this system, Eq. (18b), we obtain the analytical expressions for the Φ_k ($k = 0, 1, 2, \ldots$):

$$\Phi_1 = -(\tfrac{1}{2})\, d(\ln \Phi_0)/dR \tag{19a}$$

$$\Phi_2 = (\tfrac{1}{4})\Phi_0 d^2(\ln \Phi_0)/dR^2 - (\tfrac{1}{2})[d(\ln \Phi_0)/dR]^2, \qquad \text{etc.} \tag{19b}$$

The energy quantization condition in the complex R-plane is defined as follows (Zwaan, 1929; Kesarwani and Varshni, 1980):

$$\oint_C \Phi_0(R)\, dR + \sum_{k=2}^{\infty} (\hbar/i)^k \oint_C \Phi_k(R)\, dR = 2\pi\hbar(v + \tfrac{1}{2}) \tag{20}$$

where v is a quantum number and the term $2\pi\hbar/2$ on the right-hand side is due to the integral of $\Phi_1(R)$. The domain of R is the complex plane cut along the real R-axis between the classical turning points. The integration in Eq. (20) is carried out along a C-contour enclosing the classical turning points but no other singularities of the integrands, and not crossing the cut (Kesarwani and Varshni, 1980).

Substituting $\Phi_0(R)$, Eq. (18a), into Eq. (20) and taking into account the disappearance of all integrals with $\Phi_{2k+1}(R)$ ($k = 1, 2, \ldots$), we obtain the quantization condition up to the fourth order (Kesarwani and Varshni, 1978, 1980):

$$\begin{aligned}
&(2\mu)^{1/2} \int_{R_1}^{R_2} [E - U(R)]^{1/2}\, dR - \frac{\hbar^2}{12}(2\mu)^{-1/2} \frac{d}{dE} \int_{R_1}^{R_2} U''(R)[E - U(R)]^{-1/2} dR \\
&\quad + \frac{\hbar^4}{1440}(2\mu)^{-3/2} \frac{d^3}{dE^3} \int_{R_1}^{R_2} [7U''(R)^2 - 5U'(R)U'''(R)][E - U(R)]^{-1/2}\, dR \\
&\quad - \frac{\hbar^6}{362{,}880}(2\mu)^{-5/2} \left\{216 \frac{d^4}{dE^4} \int_{R_1}^{R_2} [U'''(R)]^2[E - U(R)]^{-1/2}\, dR \right. \\
&\quad + \frac{d^5}{dE^5} \int_{R_1}^{R_2} [93(U''(R))^3 - 224U'(R)U''(R)U'''(R) + 35(U'(R))^2U''(R)] \\
&\quad \left. \times [E - U(R)]^{-1/2}\, dR \right\} = 2\pi\hbar(v + \tfrac{1}{2})
\end{aligned} \tag{21}$$

where R_1 and $R_2(>R_1)$ are turning points.

We can write the quantization condition up to higher order terms, but where we may stop? In principle, we must include higher terms so far as the integrals in Eq. (20) can be handled, i.e., the integrals are expressed in special functions. However, this concerns the analyticity alone and the numerical procedures are unrestricted. For example, we consider the Varshni (V) potential (Varshni, 1957)

$$U_m(R) = D_e[(R_e/R)^{2m} - 2(R_e/R)^m] \tag{22}$$

The case $m = 1$ has a special interest, because $U_1(R)$ is the so-called Kratzer–Fues (or simply, Fues) potential, for which the Schrödinger equation, Eq. (15), is solved exactly, and the exact eigenvalues have the following form (Stettler and Shatas, 1971):

$$E_y(v) = -4y^2[(v + \tfrac{1}{2}) + (\tfrac{1}{4} + 4y^2)^{1/2}]^{-2}D_e \tag{23}$$

where

$$y = (R_e/2\hbar)(2\mu D_e)^{1/2} \tag{24}$$

Taking into account only the first four terms on the left-hand side of Eq. (21), one can obtain (Kesarwani and Varshni, 1980)

$$v + \tfrac{1}{2} = 2y[(1 - \omega_0^2)^{-1/2} - 1] - (1/16y) + (1/1024y^3) \tag{25}$$

where $\omega_0 = [1 + (Ey/D_e)]^{1/2}$, and Eq. (25) allows us to compare with the same expansion of the exact result, Eq. (23):

$$\begin{aligned} v + \tfrac{1}{2} = {} & 2y[(1 - \omega_0^2)^{-1/2} - 1] - (1/16y) + (1/1024y^3) \\ & - (1/32{,}768y^5) + (5/41{,}943y^7) + \cdots \end{aligned} \tag{26}$$

i.e., the approximation is very good.

Finally we summarize:

1. The Langer correction (Fröman and Fröman, 1965) is not required for diatomic potential functions, if the WKBJ calculation is carried out to the order greater than the first one (Kesarwani and Varshni, 1978).
2. The WKBJ method is more valid for the high quantum numbers than for the low ones.
3. The WKBJ method provides energy eigenvalues with very high precision for diatomic potential functions.
4. The WKBJ method enables us to obtain the approximate expression for the total number of vibrational states for a given diatomic potential function.

An alternative to the WKBJ approach is the so-called Milne approach. It is not so evident and has been recently rediscovered by Killingbeck (1980). The Milne approach is also applied to the generalization of the

WKBJ method (Hecht and Mayer, 1957) and to the study of not only bound-state energies but also quasi-bound states at resonance (complex-valued) energies (Korsch and Laurent, 1981; Korsch *et al.*, 1982). The Milne approach provides in a numerical sense a rapid second-order convergence (Korsch and Laurent, 1981). In the Milne approach the quantization condition is the same as in the WKBJ method.

The Milne approach was of course proposed by Milne (1930) and independently by Wilson (1930) and Young (1931), and is based on the following nonlinear differential equation (Milne, 1930):

$$d^2\chi(R)/dR^2 + k^2(R)\chi(R) = \chi^{-3}(R) \tag{27}$$

If some solution, $\chi = \chi(R)$, is obtained for a given $k^2(R)$, then the solution of Eq. (15) with $k^2(R) = (2\mu/\hbar^2)[E - U(R)]$ has the form

$$\Psi(R) = c\chi(R) \sin\left[\int^R \chi^{-2}(R)\, dR - b\right] \tag{28}$$

where c and b are constants.

The Milne approach is a powerful method for study of the one-dimensional Schrödinger equations involving the class of diatomic potential functions.

C. Regge Poles of Diatomic Potentials

In the following discussion we consider a very interesting aspect of diatomic interactions that is of great importance in a number of phenomena, including (1) (Connor, 1976) the rotational predissociation of diatomic molecules, (2) (Child, 1974; Stwalley, 1975) long-range behavior of diatomic interactions, (3) (Le Roy, 1973) elastic and inelastic scattering experiments, (4) three-body recombination reactions, (5) low-temperature transport properties of gases, (6) the Penning ionization, and (7) pressure-induced absorption spectra of gases. Namely, this is the theory of quasi-bound states of diatomics.

Let us consider again Eq. (15), with $U(R)$ being replaced with $U_{\text{eff}}(R, J)$, where (Berry and Mount, 1972)

$$U_{\text{eff}}(R, J) = U(R) + \hbar^2 J(J + 1)/(2\mu R^2) \tag{29}$$

and J is the orbital angular momentum quantum number. Now we assume that $U(R)$ has only one minimum at $R = R_e$. Then there exists some value of J, J_0, such that $U_{\text{eff}}(R, J_0)$ has a barrier in addition to the well determined by $U(R)$. It is easy to show that such J_0 is determined exactly by the following two relations:

$$\hbar^2 J_0(J_0 + 1)/(2\mu R_0^2) > U(R_0) \tag{30a}$$

$$\hbar^2 J_0(J_0 + 1)/(\mu R_0^3) = U'(R_0) \tag{30b}$$

where R_0 is the point where a barrier arises. This situation is depicted in Fig. 3. That barrier generates quasi-bound states of diatomics. In other words, quasi-bound states derived from Eq. (15) are defined by the following properties (de Alfaro and Regge, 1965):

$$\Psi(R = 0) = 0 \tag{31a}$$

$$\Psi(R \to \infty) \sim \text{outgoing wave } e^{ikR} \text{ alone} \qquad \text{with} \quad k = (2\mu E)^{1/2}/\hbar \tag{31b}$$

where the latter condition means that there is no incoming wave, i.e., quasi-bound states decay via tunneling through the barrier. Thus, quasi-bound states are characterized by a finite lifetime, unlike the exact bound states, which have an infinite lifetime. Commonly such quasi-bound states are called "shape resonance" [this name is from the shape of the effective potential $U_{\text{eff}}(R, J)$] or "orbiting states" because particles move in orbit around each other in the classical picture when the collision energy is close to the maximum of the barrier.

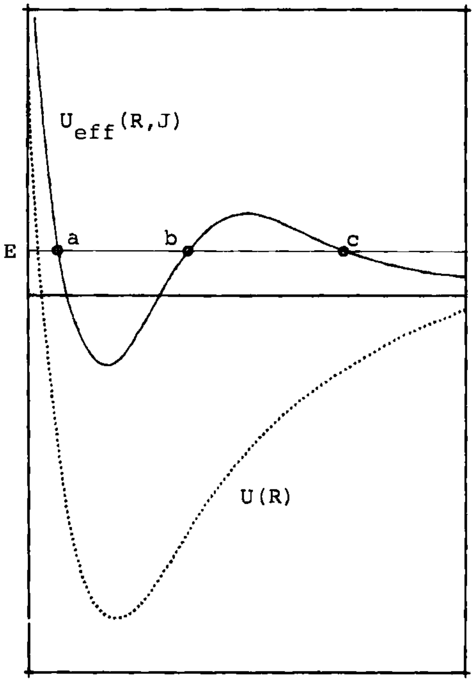


Fig. 3. Origin of quasi-bound states in diatomic interactions. Points a, b, and c are classical turning points.

The conditions imposed on $\Psi(R)$, Eq. (31), are of great importance and result in some interesting mathematical corollaries rising to the complex eigenvalue problem (de Alfaro and Regge, 1965). The problem of describing quasi-bound states is solved in two ways. The first approach consists in an assumption that J ranges physical integer values and that energy has complex values, $E_n = \varepsilon_n - \frac{1}{2}i\Gamma_n$, with $\varepsilon_n > 0$ and $\Gamma_n > 0$ ($n = 0, 1, 2, \ldots$). Traditionally, ε_n is named the resonance energy, and Γ_n is the resonance width. Thus, the system decays exponentially in time with a lifetime $\tau_n = \hbar/\Gamma_n$; a long-lived state corresponds to a small Γ_n and a short-lived one corresponds to a large Γ_n.

The complex-valued energies singled out by the boundary conditions, Eq. (31), can also be described as poles of the S-matrix. For very narrow resonances close to the real axis, the position ε_n and the width Γ_n, defined in this way, agree with other definitions based only on real energies. The most popular alternative description of resonance is undoubtedly the step-like behavior of the scattering phaseshift $\eta(E)$, where the resonance is defined by the position of the maximum of the collisional time decay function (Le Roy and Liu, 1978)

$$\tau(E) = 2h[\partial\eta/\partial E] \tag{32}$$

i.e., we have $\partial\tau/\partial E = 0$ at ε_n and the width is defined by the maximum time decay (the lifetime of the metastable state) as

$$\Gamma_n = 4h/\tau(E_n) \tag{33}$$

It is worthwhile, however, to point out that the relationship between both approaches is not one-to-one (even for sharp resonances). It has been shown for certain potentials that the phaseshift may possess a sharp, isolated Breit–Wigner-type resonance, without an S-matrix pole associated with it. The reverse situation may also be noted: a complex pole of the S-matrix does not necessarily induce a resonance-like structure in the phaseshift. Normally, however, a direct correspondence between the complex energy pole and the phaseshift characterization of resonances is observed, with good numerical agreement for sharp resonances.

In recent years the Milne method has been successfully applied to the complex energy resonances by Korsch *et al.* (Korsch and Laurent, 1981; Korsch *et al.*, 1981, 1982).

The second approach is the Regge-pole theory. In the framework of the Regge-pole theory E is considered as a real parameter, and J ranges continuous complex values, and J eigenvalues have the form

$$J_n = J_n^{(r)} + iJ_n^{(i)} \tag{34}$$

with $J_n^{(r)} > 0$ and $J_n^{(i)} > 0$, and $n = 0, 1, 2, \ldots$.

The complex eigenvalues of J are called Regge poles, and the S-matrix has the form

$$S = R_n/(J - J_n) \tag{35}$$

near a pole J, and R_n is its residue (de Alfaro and Regge, 1965).

The boundary conditions for a Regge pole

$$J = J_n(E), \qquad n = 0, 1, 2, \ldots$$

are as follows:

$$\Psi(J_n, 0) = 0 \tag{36a}$$

$$\Psi(J_n, R)_{R\to\infty} \sim \exp(ikR) \tag{36b}$$

where $k = (2\mu E)^{1/2}/\hbar$ is a wavenumber. Then S-matrix $S(J)$ is defined as (Child, 1974)

$$\Psi_{R\to\infty} \sim \exp(-ikR + \tfrac{1}{2}iJ\pi) - S(J)\exp(ikR - \tfrac{1}{2}iJ\pi) \tag{37}$$

Obviously,

$$R_n = R_n(E), \qquad J_n = J_n(E)$$

The path traced out by J_n in the complex J-plane as E varies in the interval $(-\infty, +\infty)$ is the Regge trajectory. When the boundary conditions, Eq. (36), are imposed, the Regge pole becomes complex valued with a small imaginary part (Connor, 1972), and the turning points likewise acquire small imaginary parts, if E lies below the barrier maximum of $U_{\text{eff}}(R, J)$ (see Fig. 3). As E increases, the turning points b and c become more close together until they coalesce for E equal to the barrier maximum. For large values of E, the points b and c become complex valued and at each turning point they are complex conjugates of each other.

The quantity $J_n^{(i)}$ may be physically interpreted as the inverse "angular life" of the system which decays exponentially with a scattering angle θ via $\exp(-J_n^{(i)}\theta)$ (de Alfaro and Regge, 1965). Then a long-lived state, which orbits many times before decaying, corresponds to small $J_n^{(i)}$, and for a short-lived state $J_n^{(i)}$ is large.

The semiclassical solution of Eq. (15) takes the form of

$$\Psi \sim [p(R)]^{-1/2} \exp[\pm(i/\hbar) \textstyle\int p(R)\, dR] \tag{38}$$

where $p(R)$ is usually defined as

$$p(J_n, R) = \{2\mu[E - U(R) - \hbar^2(J_n + \tfrac{1}{2})^2/(2\mu R^2)]\}^{1/2} \tag{39}$$

where we have applied the Langer substitution $(J_n + \frac{1}{2})^2$ instead of $J_n(J_n + 1)$.

Evidently, $p(J_n, R)$ is an analog of classical momentum, which is in general complex valued. Therefore, the distribution of turning points in the complex R-plane depends strongly on the nature of the potential $U(R)$. Conversely, this distribution provides the information on the nature of $U(R)$. As shown by Connor and co-workers (Connor, 1972, 1976; Connor and Mackay, 1979; Connor *et al.*, 1980), such a method provides a powerful technique for the study of diatomic interactions via comparison of the theoretical study of positions and residues of Regge poles for diatomic model potentials and the scattering experimental data.

D. Coherent States for Diatomic Energy Functions

As shown in the preceding discussions, classical (or correctly, semiclassical) arguments are very fruitful in studying the energetic behavior of diatomics. In the following discussion we present one more classical aspect, namely, the coherent-state theory. The problem of finding quantum-mechanical states, i.e., coherent states which result from the motion of a classical particle in a given potential, introduced by E. Schrödinger in 1926, has seen the great successes of Glauber (1963a,b) and Sudarshan (1963). The coherent states are defined by one of three equivalent concepts (Nieto and Simmons, 1978, 1979; Nieto, 1978):

1. Minimum uncertainty coherent states are the two-parameter set of states which minimize the position–momentum uncertainty relation, subject to the restriction that the ground state be in that set.
2. Annihilation operator coherent states are the eigenstates of the annihilation operator and are parameterized by a complex eigenvalue.
3. Displacement operator coherent states are those states which are created from the ground state by a particular unitary displacement operator.

In a series of papers, Nieto and colleagues examined in detail the problem of determining coherent states in general, and for some diatomic potential functions such as the Rosen–Morse, Morse, and Pöschl–Teller potentials (Nieto and Simmons, 1978, 1979; Nieto, 1978). The coherent-state approach is a powerful approach to study classically, i.e., at least intuitively, the energetic behavior of diatomics, and, as the authors suggest, provides the classical description of nuclear motion in diatomics.

E. Discussion

Finally we note in brief some approaches to solve a one-dimensional Schrödinger equation with a given empirical diatomic potential function. The list of empirical potential functions known from the literature is very large [see, for example, Varshni (1957), Margenau and Kestner (1971), Hirschfelder *et al.* (1964a), Claverie (1978), Goodisman (1973), Erjensoy (1965), Varshni and Shukla (1963, 1965), Nalewajski (1978a), Borkman and Parr (1968), Steele *et al.* (1962), Gosteminskaya *et al.* (1977), and references therein], and there exists approximately the same number of methods to solve them in the Schrödinger equation picture. Mainly, these methods are based on the following general approaches: (1) direct solution, (2) virial and hypervirial relations, (3) WKBJ or Milne's approach and other semiclassical methods such as the Liouville–Green technique, (4) variational approach, (5) quantum-mechanical perturbation technique, and (6) algebraic or dynamical symmetry-group method.

V. Padé Approximation of Diatomic Interactions

In Section II we discussed the Taylor series of diatomic potentials near the equilibrium separations. The Padé approach is another method to represent analytically a real diatomic potential energy function, but in recent years this powerful and elegant approach surrendered its position, probably because its force has been insufficient when applied in practice.

A. Grounds for the Padé Approach

The Padé approximant theory arose more than 90 years ago. The Padé theory is a powerful method to approximate various functions, and is successfully applied in many fields of theoretical physics and chemistry. The reason for such a success resides in, first, its more rapid convergency in comparison with the corresponding Taylor series (Baker, 1965, 1975; Baker and Gammel, 1970; Graves-Morris, 1973a,b).

Let us consider a formal power-series expansion of a given function $f(x)$ as follows:

$$f(x) = \sum_{n=0}^{\infty} a_n x^n \tag{1}$$

Definition. The Padé approximant, PA$[M/N]_f(x)$, or simply $[M/N]_f(x)$, of $f(x)$ is given by the formula

$$[M/N]_f(x) \equiv P_M(x)/Q_N(x) \tag{2}$$

where $P_M(x)$ and $Q_N(x)$ are polynomials of Mth and Nth order, respectively, and the following conditions on $P_M(x)$ and $Q_N(x)$ are imposed:

$$\text{Order}[Q_N(x)f(x) - P_M(x)] \geq M + N + 1$$

$$Q_N(0) = 1$$

which leads to

$$Q_N(x) = 1 + \sum_{i=1}^{N} q_i x^i \tag{3}$$

The definition, Eqs. (2) and (3), results in the system of linear algebraic equations (Baker, 1965, 1975; Baker and Gammel, 1970):

$$\begin{Vmatrix} a_M & a_{M-1} & \cdots & a_{M-N+1} \\ a_{M+1} & & \ddots & \vdots \\ \vdots & & & \\ a_{M+N-1} & & \cdots & a_M \end{Vmatrix} \times \begin{Vmatrix} q_1 \\ q_2 \\ \vdots \\ q_N \end{Vmatrix} = \begin{Vmatrix} a_{M+1} \\ a_{M+2} \\ \vdots \\ a_{M+N} \end{Vmatrix} \tag{4}$$

In other words, the standard Padé approximation problem (Baker, 1965, 1975; Baker and Gammel, 1970) consists in finding polynomials $P_M(x)$ and $Q_N(x)$ such that

$$P_M(x) \equiv f(x)Q_N(x) + O(x^{M+N+1}) \tag{5}$$

In a particular case with $M \geq N - 1$, the system, Eq. (4), constitutes the Toeplitz form. [In another case we put aside the definition; $a_j = 0$ for $j < 0$, and the system does not necessarily have the Toeplitz symmetry (Gilewicz and Magnus, 1979).] Let us introduce the following definition.

Definition.

$$c[M/N] \equiv \begin{vmatrix} a_{M-N+1} & a_{M-N+2} & \cdots & a_M \\ a_{M-N+2} & a_{M-N+3} & \cdots & a_{M+1} \\ \vdots & \vdots & & \vdots \\ a_M & a_{M+1} & \cdots & a_{M+N-1} \end{vmatrix} \tag{6}$$

and

$$Q[M/N](x) \equiv \begin{vmatrix} a_{M-N+1} & a_{M-N+2} & \cdots & a_M & a_{M+1} \\ a_{M-N+2} & a_{M-N+3} & \cdots & a_{M+1} & a_{M+2} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ a_M & a_{M+1} & \cdots & a_{M+N-1} & a_{M+N} \\ x^N & x^{N-1} & \cdots & x & 1 \end{vmatrix} \tag{7}$$

It is evident that the condition $c[M/N] \neq 0$ is the necessary and sufficient condition for a unique solution of Eq. (4) and, in turn, for the Padé approximation problem.

It is trivial that $c[M/N] = Q[M/N](x = 0)$. If $c[M/N] \neq 0$ then, using Cramer's rule to solve Eq. (4) and substituting it in Eq. (3), we obtain the denominator

$$Q_N(x) = Q[M/N](x)/c[M/N] \tag{8}$$

The numerator $P_M(x)$ follows from the truncation of Eq. (5) at power x^M. By this procedure, the Padé approximation problem is solved explicitly in the nondegenerate case (Baker and Graves-Morris, 1981).

Let us consider now the infinite array of the Toeplitz determinants $\{c[M/N]\}$ with the condition $c[M/0] = 1$. They are arranged in the so-called C-table

$M \backslash N$	0	1	2	$\cdots$
0	1	$c[0]$	$(c[0])^2$	
1	1	$c[1]$	$c[1/2]$	
2	1	$c[2]$	$c[2/2]$	
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\cdots$

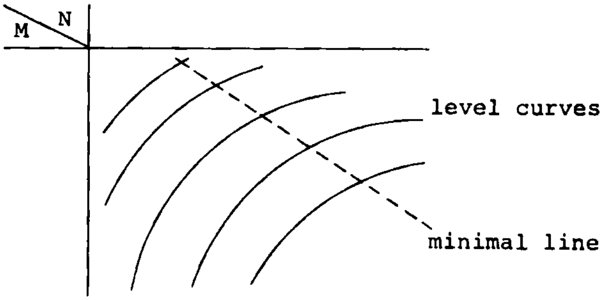
In the normal case, i.e., when for a given $c[M/N]$ its neighboring elements $c[M + 1/N + 1]$, $c[M + 1/N + 2]$, $c[M + 2/N + 1]$, etc., are different from zero, the denominator error term of the Padé approximant in some interval near $x = 0$ is given by the ratio of two Toeplitz determinants; that is

$$\{f(x) - [M/N]_f(x)\}/x^{M+N+1}|_{x=0} = (-1)^N c[M + 1/N + 1]/c[M/N] \tag{9}$$

The table of the right-hand side ratios, Eq. (9), is called the C-ratio table. Equation (9) is the basic relation in the Padé theory, and emphasizes the existence of the correlation rule between the convergence properties of Padé approximants and the internal structure of the C-table or the C-ratio table. In fact, this statement was confirmed numerically by Gilewicz (1978), who called the characteristic internal structure of the C-table "the valley structure." The valley structure is constructed by the following procedure:

1. Define the minimal line in the C-table, if it exists, as the line joining the minima of the absolute values of elements in the antidiagonals, i.e., for $M + N$ fixed (Baker and Graves-Morris, 1981).
2. Joining the quasi-equal absolute values of elements in the C-table, obtain the characteristic level curves generating the following valley

structure:



The valley structure thus defined will be very useful later when we discuss the Best Padé Approximant problem.

Finally, note that PA$[N-1/N](x)$ was examined in detail by Brändas and Goscinski (1972) in a very elegant mathematical way.

B. Padé Approach for Dunham Series

In Section I we gave some boundary conditions on the behavior of diatomic potential functions. As a standard approach, the Padé approximant, which approximates a given diatomic potential function, is chosen in such a manner that these limitations are satisfied (Jordan *et al.*, 1974; Jordan, 1975; Engelke, 1978; Yorish and Shcherbak, 1979). There exist two types of Padé approximants in the Dunham (D) version. They are as follows:

$$\text{(I)}\quad [N/N]_{\text{I}}(\xi_{\text{D}}) = a_0\xi_{\text{D}}^2\left(1+\sum_{k=1}^{N-2} a_k\xi_{\text{D}}^k\right)\bigg/\left(1+\sum_{k=1}^{N} b_k\xi_{\text{D}}^k\right) \qquad (10)$$

$$\text{(II)}\quad [N/M]_{\text{II}}(\xi_{\text{D}}) = D_e + a_0\xi_{\text{D}}^2\left(1+\sum_{k=1}^{N-2} a_k\xi_{\text{D}}^k\right)\bigg/\left(1+\sum_{k=1}^{M} b_k\xi_{\text{D}}^k\right) \qquad (11)$$

Such forms of the Padé approximants in D-version are caused by the molecular dissociation energy limit. For type I, we have only the diagonal Padé approximants. In the literature, there have been adopted two numerical procedures of finding coefficients. The first, developed by Jordan *et al.* (1974) and Jordan (1975), consists in the following procedure: The coefficients $\{a_i\}_{i=0}^{N-2}$ and $\{b_i\}_{i=1}^{N}$ are determined by the requirement that Eq. (10) must reproduce the first terms of the D-expansion. Then in that framework for $[2/2]_{\text{I}}(\xi_{\text{D}})$ and $[3/3]_{\text{I}}(\xi_{\text{D}})$ we obtain (Jordan *et al.*, 1974)

$$[2/2]_{\text{I}}(\xi_{\text{D}}) = a_0^{\text{D}}\xi_{\text{D}}^2/\{1 - a_1^{\text{D}}\xi_{\text{D}} + [(a_1^{\text{D}})^2 - a_2^{\text{D}}]\xi_{\text{D}}^2\} \qquad (12)$$

$$[3/3]_{\text{I}}(\xi_{\text{D}}) = a_0^{\text{D}}\xi_{\text{D}}^2(1 + a_1\xi_{\text{D}})/(1 + b_1\xi_{\text{D}} + b_2\xi_{\text{D}}^2 + b_3\xi_{\text{D}}^3) \qquad (13)$$

where in Eq. (13)

$$
\begin{aligned}
a_1 &= \alpha^{-1}[-2a_1^{\mathrm{D}}a_3^{\mathrm{D}} + a_4^{\mathrm{D}} - (a_2^{\mathrm{D}})^2 - (a_1^{\mathrm{D}})^4 + 3(a_1^{\mathrm{D}})^2a_2^{\mathrm{D}}] \\
b_1 &= \alpha^{-1}[a_4^{\mathrm{D}} - a_1^{\mathrm{D}}a_3^{\mathrm{D}} - (a_2^{\mathrm{D}})^2 + (a_1^{\mathrm{D}})^2a_2^{\mathrm{D}}] \\
b_2 &= \alpha^{-1}[-a_1^{\mathrm{D}}a_4^{\mathrm{D}} + a_2^{\mathrm{D}}a_3^{\mathrm{D}} + (a_1^{\mathrm{D}})^2a_3^{\mathrm{D}} - a_1^{\mathrm{D}}(a_2^{\mathrm{D}})^2] \\
b_3 &= \alpha^{-1}[-a_2^{\mathrm{D}}a_4^{\mathrm{D}} + (a_3^{\mathrm{D}})^2 + (a_1^{\mathrm{D}})^2a_4^{\mathrm{D}} + (a_2^{\mathrm{D}})^3 - 2a_1^{\mathrm{D}}a_2^{\mathrm{D}}a_3^{\mathrm{D}}] \\
\alpha &= -a_3^{\mathrm{D}} + 2a_1^{\mathrm{D}}a_2^{\mathrm{D}} - (a_1^{\mathrm{D}})^3
\end{aligned}
$$

The Jordan–Kinsey–Silbey (JKS) approach was exploited to predict spectroscopic constants for alkali halides. In particular, in the case of $[2/2]_{\mathrm{I}}(\xi_{\mathrm{D}})$, we may easily obtain the following approximations (Jordan *et al.*, 1974):

$$D_{\mathrm{e}}^{[2/2]} = a_0^{\mathrm{D}}/[(a_1^{\mathrm{D}})^2 - a_2^{\mathrm{D}}] \tag{14}$$

$$a_3^{\mathrm{D}[2/2]} = 2a_1^{\mathrm{D}}a_2^{\mathrm{D}} - (a_1^{\mathrm{D}})^3 \tag{15}$$

$$a_4^{\mathrm{D}[2/2]} = (a_2^{\mathrm{D}})^2 + (a_1^{\mathrm{D}})^2a_2^{\mathrm{D}} - (a_1^{\mathrm{D}})^4 \tag{16}$$

$$
\begin{aligned}
\gamma_{\mathrm{e}}^{[2/2]} &= (6B_{\mathrm{e}}^2/\omega_{\mathrm{e}}^2) \\
&\quad \times [5 + 10a_1^{\mathrm{D}} - 3a_2^{\mathrm{D}} - 3a_1^{\mathrm{D}}a_2^{\mathrm{D}} + (25/2)(a_1^{\mathrm{D}})^3 + (15/2)(a_1^{\mathrm{D}})^2]
\end{aligned} \tag{17}
$$

which are in good correlation with experimental data (Jordan *et al.*, 1974). Some improvement is obtained with $[3/3]_{\mathrm{I}}(\xi_{\mathrm{D}})$ in comparison with $[2/2]_{\mathrm{I}}(\xi_{\mathrm{D}})$. However, for the covalent-bonded diatomic molecules diagonal Padé approximants are not so good. The latter is easily explained by the existence, in the expansion series, Eq. (I.7), of the leading term with $n = 6$, which has much steeper behavior than does the Coulomb law describing the interaction in ionic diatomics.

The second approach for the type I approximant is based on the requirement that $[N/N]_{\mathrm{I}}(\xi_{\mathrm{D}})$ describes correctly the long-range behavior of real diatomic potentials [see Eq. (I.7)]. In particular, from the molecular dissociation energy limit one can easily obtain (Yorish and Schcherbak, 1979) $b_N = a_0a_{N-2}/D_{\mathrm{e}}$. Other relations between coefficients may be easily found from Eq. (I.7). Therefore, in contrast to the JKS-approach, in which relations on Padé coefficients are determined from the D-series, i.e., from knowledge of the behavior of a real diatomic potential near $R = R_{\mathrm{e}}$, the latter approach is based on the long-range behavior of diatomic interactions. For the harmonic consolidation of these approaches, we must apply so-called two-point Padé approximants (Barnsley, 1973; Epstein and Barnsley, 1973; Baker, 1965).

The type II approximant is a new approach completely. It is evident that this class of Padé approximant involves as a particular case type I, and the authors hope that this class, with a corresponding choice of M and N, will describe adequately covalent as well as ionic diatomics.

For example, we may write two approximants of this type:

$$\begin{aligned}[2/3]_{\mathrm{II}}(\xi_{\mathrm{D}}) &= D_{\mathrm{e}} + a_0^{\mathrm{D}}\xi_{\mathrm{D}}^2/\{1 - a_1^{\mathrm{D}}\xi_{\mathrm{D}} + [(a_1^{\mathrm{D}})^2 - a_2^{\mathrm{D}}]\xi_{\mathrm{D}}^2 \\ &\quad - [(a_1^{\mathrm{D}})^3 + 2a_1^{\mathrm{D}}a_2^{\mathrm{D}} - a_3^{\mathrm{D}}]\xi_{\mathrm{D}}^3\} \\ [4/1]_{\mathrm{II}}(\xi_{\mathrm{D}}) &= D_{\mathrm{e}} + [a_0^{\mathrm{D}}\xi_{\mathrm{D}}^2/(a_2^{\mathrm{D}} - a_3^{\mathrm{D}}\xi_{\mathrm{D}})] \\ &\quad \times \{a_2^{\mathrm{D}} + (a_1^{\mathrm{D}}a_2^{\mathrm{D}} - a_3^{\mathrm{D}})\xi_{\mathrm{D}} + [(a_2^{\mathrm{D}})^2 - a_1^{\mathrm{D}}a_3^{\mathrm{D}}]\xi_{\mathrm{D}}^2\} \qquad (18)\end{aligned}$$

Therefore, the Dunham version of the Padé technique is very useful in comparison with some other expansion approaches, in particular with the SPF-approach. This was mentioned by Jordan (1975). Engelke (1978) also showed that the Dunham version of the Padé approximants provides slightly better approximations than does the OT-expansion for $R > R_{\mathrm{e}}$, and for $R < R_{\mathrm{e}}$ they are virtually identical approximations. At the same time, the D-version of the Padé technique has its shortcomings, which explains the lower level of confidence in its application to diatomic potential theory. One of these, and, in our opinion, the most essential, consists in choosing only diagonal Padé approximants (type I), i.e., all power of the Padé approach is off-side of our interest. Such diagonal approximants are historically suggested by Stieltjes, and, as proved by Baker (1975; [Theorem 15.2]), $[N/N]$ approximants form the best upper bounds for the Stieltjes series. However, in general, it is not known if any potential energy function $U(R)$ is the Stieltjes series. If this is the case, then we shall obtain the grounds for using only diagonal Padé approximants in the D-version. Otherwise, we must solve the Best Padé Approximant problem and construct the best Padé approximants.

C. Poles of Padé Approximants

In the preceding discussion we have constructed diagonal $[N/N]_{\mathrm{I}}(\xi_{\mathrm{D}})$ Padé approximants in the framework of the JKS-approach. In the Padé approximant approach to diatomic potentials, however, there exists an essential disadvantage connected with poles of Padé approximants, i.e., zeros of denominator. In particular, for $N = 2$ the poles of the Padé approximants are all situated at complex R, for the real part of R being negative; in the case of $N = 3$, $[3/3]_{\mathrm{I}}(\xi_{\mathrm{D}})$ has no poles for real and positive ξ_{D}. Therefore, the problem of finding zeros of a given Padé approximant is of great importance in diatomic potential theory. The essential advances to solve this problem have been made recently by Brändas and Goscinski (1972) and Leopold (1982) (see also references therein). It is evident that this problem becomes more complex for $[M/N]$ approximants with $N \geq 5$, where the general numerical algorithm for finding zeros of $Q_N(x)$ does not exist. So we give some statements without any proofs, which serve as an initial stage of the study of poles of approximants. In our opinion, these statements will be useful for researchers to avoid spurious results. They are as follows:

THEOREM 1 (Leopold, 1982). Let $\{Q_N\}_{N \geq 0}$ be a sequence of degree N polynomials which satisfy the recurrence relation

$$Q_{N+1}(\xi) = (b_N + b'_N\xi)Q_N(\xi) - A_N(\xi)Q_{N-1}(\xi) \qquad (19)$$

where $b'_N > 0$, $N = 0, 1, 2, \ldots, L - 1$; $Q_1(\xi) \equiv 0$; $Q_0(\xi) \equiv q_0 \neq 0$; and $A_N(\xi)$ are the polynomials of degrees not exceeding 2 ($N = 1, 2, \ldots$) with $A_0(\xi) \equiv 1$. Then this family $\{Q_N\}$ has no zeros in the region $\mathcal{R}_N$ defined as follows:

$$\mathcal{A}_L = \{\xi \in \mathbf{C} | A_N(\xi) \neq 0, \qquad N = 0, 1, \ldots, L - 1\}$$

$$0 \leq N < L - 1: \quad b_N(\xi, d) = [|A_{N+1}(\xi)| + \operatorname{Re} A_{N+1}(\xi)]/[2b'_N(\operatorname{Re} \xi - d)]$$

$$\tilde{b}_N(\xi, d) = [|A_{N+1}(\xi)| - \operatorname{Re} A_{N+1}(\xi)]/[2b'_N(\operatorname{Im} \xi - d)]$$

$$0 \leq N < L: \quad g_N(d) = \operatorname{Re} b_N + b'_N d, \qquad \tilde{g}_N(d) = \operatorname{Im} b_N + b'_N d$$

$$I_{1,N} =]\max_{0<N<L}[-\operatorname{Re} b_N/b'_N], +\infty[\bigcap [-\operatorname{Re} b_0/b'_0, +\infty]$$

$$I_{2,N} =]-\infty, \min_{0<N<L}[-\operatorname{Re} b_N/b'_N][\bigcap [-\infty, -\operatorname{Re} b_0/b'_0]$$

$$I_{3,N} =]\max_{0<N<L}[-\operatorname{Im} b_N/b'_N], +\infty[\bigcap [-\operatorname{Im} b_0/b'_0, +\infty]$$

$$I_{4,N} =]-\infty, \min_{0<N<L}[-\operatorname{Im} b_N/b'_N][\bigcap [-\infty, -\operatorname{Im} b_0/b'_0]$$

$$\mathcal{R}_{1,N} = \bigcup_{d \in I_{1,N}} \left\{ \bigcap_{0 \leq N < L-1} \{\xi \in \mathcal{A}_N | b_N(\xi, d) \leq g_{N+1}(d), \operatorname{Re} \xi > d\} \right\}$$

$$\mathcal{R}_{2,N} = \bigcup_{d \in I_{2,N}} \left\{ \bigcap_{0 \leq N < L-1} \{\xi \in \mathcal{A}_N | b_N(\xi, d) \geq g_{N+1}(d), \operatorname{Re} \xi < d\} \right\}$$

$$\mathcal{R}_{3,N} = \bigcup_{d \in I_{3,N}} \left\{ \bigcap_{0 \leq N < L-1} \{\xi \in \mathcal{A}_N | \tilde{b}_N(\xi, d) \leq \tilde{g}_{N+1}(d), \operatorname{Im} \xi > d\} \right\}$$

$$\mathcal{R}_{4,N} = \bigcup_{d \in I_{4,N}} \left\{ \bigcap_{0 \leq N < L-1} \{\xi \in \mathcal{A}_N | \tilde{b}_N(\xi, d) \geq \tilde{g}_{N+1}(d), \operatorname{Im} \xi < d\} \right\}$$

and

$$\mathcal{R}_N = \bigcup_{1 \leq i \leq 4} \mathcal{R}_{i,N}$$

THEOREM 2 (Leopold, 1982). Let the same as in Theorem 1 be given, and in addition $A_N(\xi) = a_N\xi$, and a_N and b'_N are positive real numbers, and b_N are real numbers. Let us define sets $\Gamma_{i,N}$ ($i = 1, 2, 3, 4$) as follows:

$$\Gamma_{1,N} = \bigcup_{d\ge -b_0/b'_0} \underset{\substack{d>\max(-b_N/b'_N)\\ 0<N<L}}{\Big\{} \xi \in \mathbf{C} \quad |\phi(\xi, d) \le \min_{0<N<L} \psi_N(d),\ \operatorname{Re}\xi > d\Big\}$$

$$\Gamma_{2,N} = \bigcup_{d\le -b_0/b'_0} \underset{\substack{d<\min(-b_N/b'_N)\\ 0<N<L}}{\Big\{} \xi \in \mathbf{C} \quad |\phi(\xi, d) \ge \max_{0<N<L} \psi_N(d),\ \operatorname{Re}\xi < d\Big\}$$

$$\Gamma_{3,N} = \bigcup_{d>0} \{\xi \in \mathbf{C} | \tilde{\phi}(\xi, d) \le \min_{0<N<L} \tilde{\psi}_N(d),\ \operatorname{Im}\xi > d\}$$

$$\Gamma_{4,N} = \bigcup_{d<0} \{\xi \in \mathbf{C} | \tilde{\phi}(\xi, d) \ge \max_{0<N<L} \tilde{\psi}_N(d),\ \operatorname{Im}\xi < d\}$$

where we have put on

$$\phi(\xi, d) = (|\xi| + \operatorname{Re}\xi)/2(\operatorname{Re}\xi - d)$$

$$\tilde{\phi}(\xi, d) = (|\xi| - \operatorname{Re}\xi)/2(\operatorname{Im}\xi - d)$$

and for $0 < N < L$

$$\psi_N(d) = (b'_{N-1}/a_N)(b_N + b'_N d)$$

$$\tilde{\psi}_N(d) = (b'_{N-1} b_N/a_N)\, d$$

Then the region Γ_N defined by

$$\Gamma_N = \bigcup_{1\le i\le 4} \Gamma_{i,N}$$

contains no zeros of the family $\{Q_N\}_{N=0}^{L-1}$.

THEOREM 3 (Leopold, 1982). Assume that in Eq. (19) we have $A_N(\xi) \equiv a_N$ for all $N (0 \le N < L)$, and a_N and b'_N are positive real numbers, and b_N are real numbers. Let us define

$$\forall\ \xi \le \xi_1 = \min_{0\le N<L}(-b_N/b'_N): \qquad m(\xi) = \min_{0<N<L}(a_N/b'_{N-1})(b_N + b'_N\xi)^{-1}$$

$$\forall\ \xi \ge \xi_2 = \max_{0\le N<L}(-b_N/b'_N): \qquad M(\xi) = \max_{0<N<L}(a_N/b'_{N-1})(b_N + b'_N\xi)^{-1}$$

Then the polynomial Q_N with $N = 1, 2, \ldots, L$ has all its zeros in the open interval I_N defined by

$$I_N = (\max_{\xi\le\xi_1}[\xi + m(\xi)],\ \min_{\xi\ge\xi_2}[\xi + M(\xi)])$$

D. Discussion

First, we emphasize some convergence properties of Padé approximants. In this connection the approach proposed by Johnson (1971) is of great interest. He proved that for convergent series Padé approximants accelerate the convergence, while for divergent power series they estimate it [see also Basdevant (1971)]. This approach may have a great importance in improving the convergence in the diatomic potential theory. There are a large number of mathematical examples in which the convergence of Padé approximants has not been proved, but numerical computations indicate that they do converge. Nevertheless, Baker and Gammel proved that there exist subsequences of diagonal Padé approximants which converge uniformly on any compact set in the convergence circle of the Taylor series (Baker and Gammel, 1961).

Second, we consider transformation properties of the Padé approximants. Following Basdevant (1971), we may ask "What are the transformation properties which are common to the function $f(x)$, Eq. (1), and its Padé approximants, since the Padé algorithm is nonlinear?"

Let us consider a homographic transformation on the variable x which leaves the origin invariant, because we expand near this point, $x = 0$:

$$x = \alpha x'/(1 + \beta x') \tag{20}$$

Basdevant (1971) proved that for a particular case of diagonal Padé approximants, the transformed approximant is the approximant of the transformed function $f(\alpha x'/(1 + \beta x'))$. Therefore, Padé approximants preserve homographic transformation properties of the x variable. This property is of fundamental importance and may be very useful for analytical representation of real diatomic potentials. It is evident that the transformation given by Eq. (20) is the same one that we considered in Section II [Eq. (II.17)] to emphasize the unified approach between various power-series expansions that are known in the literature. In modern state-of-the-art diatomic potential theory, this fundamental property of the Padé approximants has not been taken into account. In our opinion, this property may serve as a new basis in advancing the Padé approach to diatomic potential theory. Moreover, a given transformation property may be also used with respect to the following aspects (Basdevant, 1971). First, this property can be used to relate $[N \pm 1/N]$ with $[N/N]$ and, in particular, to obtain the Padé coefficients recurrently from the Taylor series (Baker, 1965; Zinn-Justin, 1971). Second, taking into account this property, the poles are not to be considered as special points for Padé approximants, as opposed to the Taylor series, since one can in all cases normalize them by corresponding suitable homographic transformations. Also, in particular, we may choose α and β from Eq. (20) in terms of the coefficients a_n in Eq. (1) in the most efficient way, which is very important for the convergence.

Finally, we would like to make some mention of the Best Padé Approximant problem. Earlier we referred to the most general Padé approximants, not only to diagonal ones. Then, naturally, the practical question will arise (Gilewicz, 1981a): "Well, the Padé approximant is good, but which one is better?" The main problem in the Padé theory is the convergence property of the Padé approximant. In computational applications, however, the main problem is quite different, namely, how to choose a good Padé approximant derived from a finite set of Padé approximants, which can be handled. And what do we mean by "good"? This is the essence of the Best Padé Approximant problem. This problem is discussed by many authors [see Gilewicz (1981a), Graves-Morris (1979a), and references therein]. This is a rather complicated problem. Note that recently Gilewicz (1981b) has suggested a new algorithm to solve this problem which is based on the valley structure of the *C*-ratio table (see Section V,A).

Finally we note that we have not been concerned with all applications of the Padé approximant approach to diatomic potential theory (Epstein, 1968; Brändas and Micha, 1972; Barnsley and Aguilar, 1978; Goscinski and Tapia, 1972; Sullivan, 1978; Thakkar, 1978), but we have discussed here only the aspects of the Padé approach that, in our opinion, will have fundamental value in diatomic potential theory and will elevate the theory of Padé to a level of distinction such as it deserves.

VI. Virial Theorem and Its Implications

A. General Considerations

The virial theorem provides a powerful tool to study diatomic potential energy functions, in particular, to carry out the analysis of the components of the Born–Oppenheimer diatomic energy, such as the total Coulombic potential energy and the total kinetic energy of electrons, and their contributions to the bonding in diatomics (Löwdin, 1959; Clinton, 1960, 1963; Clinton and Frattati, 1962; Steele *et al.*, 1962; Ruedenberg, 1962; Parr and Borkman, 1967; Borkman and Parr, 1968; Parr and Brown, 1968; Nalewajski, 1977; Nalewajski and Parr, 1977; Winn, 1981; Kryachko, 1983d,e).

Let $U_n(R)$ be the total Born–Oppenheimer energy for a given diatomic system in its *n*th electronic state, and $T_n(R) \equiv \langle n|T|n\rangle$ and $V_n(R) \equiv \langle n|V|n\rangle$ are the corresponding electronic kinetic and potential functions. Evidently, these are functions of the internuclear distance *R* (Slater, 1963).

The virial theorem states

$$T_n(R) = -U_n(R) - R[dU_n(R)/dR] \tag{1}$$

and

$$V_n(R) = 2U_n(R) + R[dU_n(R)/dR] \tag{2}$$

From Eq. (1) one can easily obtain (Clinton, 1963) that

$$-[dT_n/dR] = R^2[d^2U_n/dR^2] + 2[dU_n/dR] \tag{3}$$

After some elementary mathematical calculations, carried out by Clinton (1963), one can obtain the second-order differential relation on $U_n(R)$:

$$R^2[d^2U_n/dR^2] + 2R[dU_n/dR] - 2T_n = 2S_n \tag{4}$$

where

$$S_n(R) \equiv \sum_{m\neq n} |\langle n|T|m\rangle|^2/[U_n(R) - U_m(R)] \tag{5}$$

Notice that the same equation, Eq. (4), had been also obtained by Byers-Brown (1958).

Taking into account Eq. (1), we obtain finally

$$R^2[d^2U_n/dR^2] + 4R[dU_n/dR] + 2U_n = 2S_n \tag{6}$$

Naturally, one can consider Eq. (6) as a second-order linear inhomogeneous equation to find $U_n(R)$. Its solution is given in quadrature, and the general solution of the homogeneous part of Eq. (6) has the form

$$U_n(R) = A_n/R + B_n/R^2 \tag{7}$$

where A_n and B_n are constants. However, in general, the function $S_n(R)$ is unknown. [If we consider A_n and B_n as a function of R, then from Eq. (6) we obtain the relation: $R[d^2A_n/dR^2] + 2[dA_n/dR] + [d^2B_n/dR^2] = 2S_n$.] Nevertheless, one can make some statements about the behavior of $S_n(R)$. They are as follows (Clinton, 1963):

$$S_n(0) = W_n(0) = -T_n(0) \tag{8a}$$

$$S_n(\infty) = W_n(\infty) = -T_n(\infty) \tag{8b}$$

In particular, for $n = 0$, i.e., for the nondegenerate ground state, $U_0(R) < U_m(R)$ for all m and R. Then the inequality holds: $S_0(R) < 0$, and

$$R^2[d^2U_0/dR^2] + 4R[dU_0/dR] < -2U_0 \tag{9}$$

For $R = R_e$ it follows

$$d^2U_0(R)/dR^2|_{R=R_e} < 2|U_0(R_e)|R_e^2 \tag{10}$$

Therefore, there exist two alternative possibilities. The first one is a positive sign of $U_0''(R_e)$, and the second one consists in a negative sign of $U_0''(R_e)$. Thus, the virial theorem does not exclude from the realm of possibilities the existence of more than one type of equilibrium position R_e. The problem of the number of equilibrium positions has not yet been solved in general.

Now we define the S-matrix with elements (Clinton, 1963):

$$S_{nm}(R) \equiv |\langle n|T|m\rangle|^2/[U_n(R) - U_m(R)] = -S_{mn}(R) \tag{11}$$

Namely, the S-matrix is antisymmetric and $S_{nn} = 0$. Then $S_n(R) = \sum_m S_{nm}(R)$ and $\sum_n S_n(R) = 0$ for all R. If we denote $w(R)$ as the sum $\sum_n U_n(R)$, then Eq. (6) is rewritten for $w(R)$ as follows:

$$R^2[d^2w/dR^2] + 4R[dw/dR] + 2w = 0 \tag{12}$$

which has a solution of the type

$$w(R) = \mathcal{A}/R + \mathcal{B}/R^2 \tag{13}$$

Thus, we may state that for any $U_n(R)$ there exist some blocks of the type seen in Eq. (13).

Definition. The Clinton function $\alpha(R)$ is defined as follows:

$$\alpha_n(R) \equiv -S_n(R)/T_n(R) \tag{14}$$

In terms of $\alpha_n(R)$, Eq. (6) becomes

$$R^2[d^2U_n/dR^2] + 2(2 - \alpha_n)R[dU_n/dR] + 2(1 - \alpha_n)U_n = 0 \tag{15}$$

Recently, Kryachko (1983a,b) applied the Clinton function $\alpha_n(R)$ as a test for finding the applicability range of the model diatomic potentials. The Clinton function is directly connected with the kinetic energy function, and therefore is also applied as a test function for $T_n(R)$, since the knowledge of $T_n(R)$ is of general interest in discussing the dynamical behavior of diatomics and estimating corrections to the Born–Oppenheimer approximation (Stwalley, 1973c), and also in studying the vapor-pressure isotopic effects (Phillips *et al.*, 1972; Present, 1973). In this connection we must note that the need for obtaining new tests of validity of model diatomic potential functions is actually growing, and it also concerns the test of the so-called general principles which, in particular, does not require cumbersome calculations such as, for example, the test based on the comparative analysis with the experimental second virial coefficient. Note that such tests are not common in the literature. Here one should point to the papers by Erjensoy (1965) and Brown and Rowlinson (1960), based on the virial theorem, and also the paper by Thakkar and Smith (1977) on the behavior of $n(R)$-6 potential for large R. Applying the α_n test, Kryachko (1983b) determined the range of validity of some widely used practical model diatomic functions, such as the Lennard–Jones, Varshni, Lifson (Abraham and Stölevik, 1978), Varshni–Shukla (Varshni and Shukla, 1965), and their particular cases: the Born–Mayer, Wasastjerna, Hellmann, and Varshni–Shukla-II potentials, and the Morse, 6-exp Buckingham, Frost–Musulin, Rydberg, and Nalewajski (Nalewajski, 1978a) functions.

B. Potential and Kinetic Energy Components

In Section VI,A, we have obtained via the virial theorem the general formulas for the kinetic and potential energy components, Eqs. (1) and (2), which give the expectation values averaged on the electron subsystem. These quantities are of great importance in the theory of diatomic molecules, in particular, in the study of the dynamical behavior of diatomics (Levine, 1974), and in estimating the corrections to the Born–Oppenheimer approximation (Le Roy and Bernstein, 1968). The semiclassical expressions of such quantities are determined from the vibrational spacing in a simple way, as demonstrated by Stwalley (1973c). These results are in excellent agreement with the exact quantum mechanical values for diatomics.

The classical expectation value of the kinetic energy, $T = p^2/2\mu$, is written in the following form (Stwalley, 1973c):

$$\langle T \rangle = \oint T(t)\, dt \Big/ \oint dt \tag{16}$$

Introducing the variable Q and putting $dQ = (p/\mu)\, dt$, Eq. (16) is transformed to

$$\langle T \rangle = (1/2) \oint p\, dQ \Big/ \oint (\mu/p)\, dQ \tag{17}$$

Then taking into account the quantization condition of $(1/2\pi) \oint p\, dQ = (v + \frac{1}{2})$ (Section IV), we obtain finally (Stwalley, 1973c)

$$\langle T \rangle = \tfrac{1}{2}(v + \tfrac{1}{2})[dE/d(v + \tfrac{1}{2})] = \tfrac{1}{2}[dE/d\tau(v + \tfrac{1}{2})] \tag{18}$$

where τ is a vibration period. By analogy, for the potential energy component one can derive (Stwalley, 1973c)

$$\langle V \rangle = E - \langle T \rangle = E - \tfrac{1}{2}[dE/d\tau(v + \tfrac{1}{2})] \tag{19}$$

In a particular case of rotationless energy levels, applying the Dunham formula [Eq. (II.7)], $\langle T \rangle$ and $\langle V \rangle$ become

$$\langle T \rangle = (1/2) \sum_{n=1}^{\infty} n Y_{n0} (v + \tfrac{1}{2})^n \tag{20a}$$

and

$$\langle V \rangle = \sum_{n=1}^{\infty} (1 - n/2) Y_{n0}(v + \tfrac{1}{2})^n \tag{21a}$$

or, in spectroscopic notation,

$$\langle T \rangle = \tfrac{1}{2}\{\omega_e(v + \tfrac{1}{2}) - 2\omega_e x_e(v + \tfrac{1}{2})^2 + 3\omega_e y_e(v + \tfrac{1}{2})^3 + \cdots\} \tag{20b}$$

and

$$\langle V \rangle = D_e + \tfrac{1}{2}\{\omega_e(v + \tfrac{1}{2}) - \omega_e y_e(v + \tfrac{1}{2})^3 + \cdots\} \tag{21b}$$

From Eqs. (20b) and (21b) it follows that $\langle T \rangle \rightarrow 0$ and $\langle V \rangle \rightarrow D_e$ as $v \rightarrow -\frac{1}{2}$.

Above we have considered the bottom region of the well, or small values of v. On the other side, in the dissociation limit, we have [Eq. (IV.2)] (Stwalley, 1973c)

$$\langle T \rangle = [n/(n - 2)] X_n(0)(v + \tfrac{1}{2})(v_D - v)^{(n+2)/(n-2)} \tag{22a}$$

and

$$\langle V \rangle = -X_n(0)(v_D - v)^{2n/(n-2)}\{1 + [n(v + \tfrac{1}{2})/(n - 2)(v_D - v)]\} \tag{22b}$$

And again we can derive the limits: $\langle T \rangle \rightarrow 0$ and $\langle V \rangle \rightarrow 0$ as $v \rightarrow v_D$. It is not difficult to write $\langle T \rangle$ and $\langle V \rangle$ in the intermediate v region using the formula by Beckel and co-workers (Beckel *et al.*, 1970; Hashemi-Attar *et al.*, 1979; Hashemi-Attar and Beckel, 1979) [Eq. (IV.9)].

The generalization of the results presented to the general case of vibrational–rotational levels is evident (Stwalley, 1973c):

$$\langle T \rangle = (1/2) \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} n Y_{nm}(v + \tfrac{1}{2})^n [J(J + 1)]^m \tag{23a}$$

and

$$\langle V \rangle = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (1 - n/2) Y_{nm}(v + \tfrac{1}{2})^n [J(J + 1)]^m \tag{24a}$$

or, in spectroscopic notation

$$\begin{aligned} \langle T \rangle = {} & \tfrac{1}{2}\{\omega_e - \alpha_e[J(J + 1)] - \beta_2[J(J + 1)]^2 + \cdots\}(v + \tfrac{1}{2}) \\ & + \{-\omega_e x_e + \gamma_e[J(J + 1)] + \cdots\}(v + \tfrac{1}{2})^2 \\ & + \tfrac{3}{2}\{\omega_e y_e + \cdots\}(v + \tfrac{1}{2})^3 + \cdots \\ \equiv {} & \tfrac{1}{2}[\omega_e^J(v + \tfrac{1}{2}) - 2\omega_e x_e^J(v + \tfrac{1}{2})^2 + 3\omega_e y_e^J(v + \tfrac{1}{2})^3 + \cdots] \end{aligned} \tag{23b}$$

and

$$\begin{aligned}\langle V\rangle &= D_e + \tfrac{1}{2}\{\omega_e - \alpha_e[J(J+1)] - \beta_e[J(J+1)]^2 + \cdots\}(v+\tfrac{1}{2})\\ &\quad - \tfrac{1}{2}\{\omega_e y_e + \cdots\}(v+\tfrac{1}{2})^3 + \cdots\\ &\equiv D_e + \tfrac{1}{2}\{\omega_e^J(v+\tfrac{1}{2}) - \omega_e y_e^J(v+\tfrac{1}{2})^3 + \cdots\}\end{aligned} \tag{24b}$$

where

$$\omega_e^J = \sum_{m=0}^{\infty} Y_{1m}[J(J+1)]^m$$

$$\omega_e x_e^J = \sum_{m=0}^{\infty} Y_{2m}[J(J+1)]^m$$

$$\omega_e y_e^J = \sum_{m=0}^{\infty} Y_{3m}[J(J+1)]^m$$

and so on. Therefore, we have derived the v-dependence of the kinetic and potential energy components in both limiting cases for small v and for $v \to v_D$. These results are easily rewritten in terms of mass-reduced quantum numbers (Stwalley, 1971):

$$y = (v+\tfrac{1}{2})\mu^{-1/2}$$

and

$$\xi = [J(J+1)]\mu^{-1}$$

Let us consider Eq. (1) again. The kinetic energy function $T_n(R)$ has the following properties (Kryachko, 1983e):

1. $T_n(0) = -W_n(0)$, where $W_n(0)$ is the energy of the united atom.
2. $T_n(\infty) = -U_n(\infty)$.
3. $T_n(R)$ has a minimum at $R = R_0$. This is confirmed by the exact calculations by Kolos and Wolniewicz for H_2 (Kolos and Wolniewicz, 1965).
4. $T_n(R_e) = -U_n(R_e)$ as a corollary of the virial theorem.
5. $T_n(R)$ satisfies the so-called normalization condition (Fig. 4) (Nalewajski, 1978b):

$$\int_0^{\infty}[T_n(R) - T_n(\infty)]\,dR = Z_A Z_B \tag{25}$$

From Eqs. (1) and (25) directly follows the integral form of the virial theorem (Nalewajski, 1978b):

$$U_n(R) = (1/R)[Z_A Z_B - \int_0^R T(R')\,dR'] \tag{26}$$

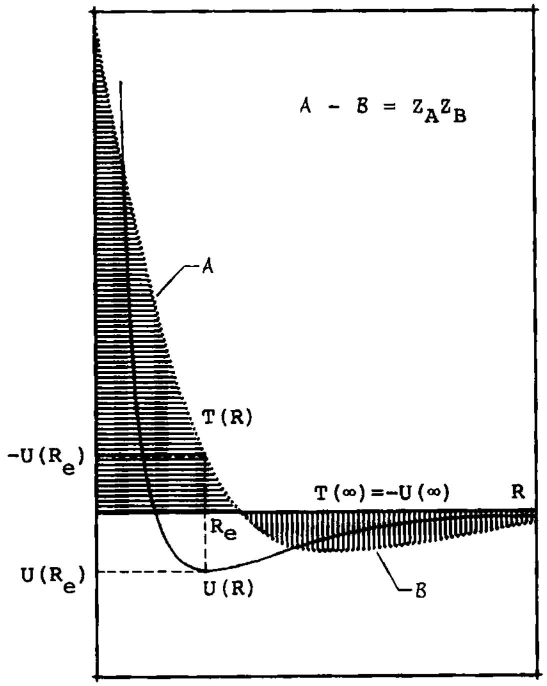


Fig. 4. The kinetic energy function $T(R)$ for a stable electronic state of a diatomic molecule and the normalization condition Eq. (25).

Substituting in Eq. (15) the expression for $U_n(R)$ from Eq. (26), we obtain the differential relation for the kinetic energy function $T_n(R)$ (Kryachko, 1983b):

$$R[dT_n/dR] + 2(1 - \alpha_n)T_n = 0 \tag{27}$$

Let $T_n(R)$ have the minimum at $R = R_0^{(n)}$. From Eq. (27) it follows that $\alpha_n(R_0^{(n)}) = 1$, and also the following interesting expression results:

$$T_n(R_0^{(n)}) = \sum_{m \neq n} |\langle n|T|m\rangle|^2/[U_m(R) - U_n(R)]|_{R=R_0^{(n)}}$$

which, in a particular case of $n = 0$, has been proved by Davidson (1962). Assuming that the function $\alpha_n(R)$ is known we proceed to the following discussion.

C. Construction Procedure for Diatomic Potential Functions

Now, if $\alpha_n(R)$ is known, then Eq. (27) becomes a linear first-order differential equation for $T_n(R)$ (Step I); solving it we obtain $U_n(R)$ via Eq.

(26) (Step II). All is very simple, but inconsistency arises: we need to know $\alpha_n(R)$. We may turn to Step I, and substitute some expressions for $T_n(R)$ satisfying the known conditions to obtain $U_n(R)$ via Eq. (26). This approach, suggested by Nalewajski (Nalewajski, 1978c; Kryachko, 1983c), is very elegant. Nalewajski (1978c) approximated $T_n(R)$ by some well-known functions—Morse, Rydberg, Rosen–Morse, and Hulbert–Hirschfelder (Varshni, 1957)—and derived the expressions for $U_n(R)$ (Table IV). The tests for such modified diatomic potentials demonstrated their force and reliability. However, we would like to note that nothing from these analytical models for $T_n(R)$ satisfies the normalization condition: the only exception is the Frost–Musulin potential, which has not been considered as a substitute for $T_n(R)$.

The overall procedure, involving Step I and Step II, is very complex. The main goal consists in guessing the correct $\alpha_n(R)$ [see, for example, Kryachko (1983b)], but is not so simple. A more simple approach is to expand $\alpha_n(R)$ around some point, for example, around $R = R_e$ or $R = 0$, in the Taylor series, or to represent $\alpha_n(R)$ as a corresponding Padé approximant. The expansion of $\alpha_n(R)$ in the Taylor series at $R = R_e$ provides only poor representation for the real behavior of $U_n(R)$. The Padé approach gives better results. In the particular case of the Fues potential (Fues, 1926) [Eq. (VIII.18)], $\alpha_F(R)$ has the following form:

$$\alpha_F(R) = 2U_0R^2/(U_0R^2 - U_2) \tag{28}$$

i.e., $\alpha_F(R)$ is represented by the Padé approximant of the type $[0/1](R^{-2})$. A better description provides the modified Fues potential, proposed independently by Clinton (Clinton, 1962; Kryachko, 1983d) using the Taylor series expansion for $\alpha(y(R))$ where $y = \ln(R/R_e)$, and by Nalewajski (1977) via the Parr–White perturbation approach (Parr and White, 1968). The Clinton–Nalewajski (CN) diatomic function takes the following form:

$$U_{CN}(R) = U_0 + U_1(R_e/R) + U_2(R_e/R)^2 + U_3(R_e/R)\ln(R_e/R) \tag{29}$$

which involves a logarithmic term in addition to the Fues potential. In this case, for the Clinton function $\alpha(R)$, one can obtain

$$\alpha_{CN}(R) = (2U_0R^2 - U_3R_eR)/(U_0R^2 - U_2R_e^2 - U_3R_eR) \tag{30}$$

which is a Padé approximant:

$$\alpha_{CN}(R) = [1/2](R^{-1}) \tag{31}$$

Given higher order Padé approximants, one can obtain the exact description of $U(R)$ up to a fourth-order force constant k_4 (Rossikhin and Morozov, 1983; Kryachko, 1983c–e).

TABLE IV

MODIFIED POTENTIAL ENERGY FUNCTIONS[a] $[U(\infty) = -T(\infty) \equiv 0]$

Form of the kinetic energy function; $x = R - R_0$	Modified energy function via Eq. (26)	Normalization condition Eq. (25)
Morse (M) $T_M(R) = a(e^{-2cx} - 2e^{-cx})$	$U_M(R) = \dfrac{a}{2cR}(e^{-2cx} - 4e^{-cx})$	$\dfrac{a}{2c}(e^{2cR_0} - 4e^{cR_0}) = Z_A Z_B$
Rydberg (R) $T_R(R) = -a(1 + cx)e^{-cx}$	$U_R(R) = \dfrac{a}{R}\left(R_0 - \dfrac{2}{c} - R\right) e^{-cx}$	$ae^{cR_0}\left(R_0 - \dfrac{2}{c}\right) = Z_A Z_B$
Rosen–Morse (RM) $T_{RM}(R) = A\left[\tanh\left(\dfrac{R}{d}\right) - 1\right] - C\,\mathrm{sech}^2\left(\dfrac{R}{d}\right)$	$U_{RM}(R) = \dfrac{d}{R}\left\{A\left[\dfrac{R}{d} - \ln\left(2\cosh\left(\dfrac{R}{d}\right)\right)\right] + C\left[\tanh\left(\dfrac{R}{d}\right) - 1\right]\right\}$	$-d(C + A\ln 2) = Z_A Z_B$
Hulburt–Hirschfelder (HH) $T_{HH}(R) = T_M(R) + dc^3x^3e^{-2cx}(1 + cfx)$	$U_{HH}(R) = -\dfrac{2a}{cR}e^{-cx} + \dfrac{1}{cR}\left\{\dfrac{a}{2} + \dfrac{d}{8}[4fy^4 + (1 + 2f)(4y^3 + 6y^2 + 6y + 3)]\right\} \times e^{-2cx}; \quad y = cx$	$-\dfrac{2a}{c}e^{cR_0} + \left\{\dfrac{a}{2} + \dfrac{d}{8}[4f(cR_0)^4 + (1 + 2f)[-4(cR_0)^3 + 6(cR_0)^2 - 6(cR_0) + 3]]\right\}\dfrac{1}{c} \times e^{2cR_0} = Z_A Z_B$

[a] Nalewajski (1978c).

VII. Force Concept Analysis for Diatomic Interactions

In the preceding sections we have studied diatomic interactions via $U(R)$. However, the study of diatomic interactions can also be carried out in terms of the force $F(R)$ instead of the energy $U(R)$, where R denotes the internuclear separation. Though there are several methods for the calculation of the force, the electrostatic theorem of Hellmann (1937) and Feynman (1939) is of particular interest in this section, since the theorem provides a simple and pictorial method for the analysis and interpretation of interatomic interactions based on the three-dimensional distribution of the electron density $\rho(\mathbf{r})$. An important property of the Hellmann-Feynman (HF) theorem is that underlying concepts are common to both the exact and approximate electron densities (Epstein *et al.*, 1967, and references therein). The force analysis of diatomic interactions is a useful semiclassical and therefore intuitively clear approach. And this results in the analysis of diatomic interactions via force functions instead of potential ones (Clinton and Hamilton, 1960; Goodisman, 1963). At the same time, in the authors' opinion, it serves as a powerful additional instrument to reexamine model diatomic potential functions.

A. Concept of Hellmann–Feynman Force

The time derivative of an operator A can be defined by [see, for example, Merzbacher (1961)]

$$dA/dt = i[H, A] + \partial A/\partial t \tag{1}$$

where square brackets denote the commutator $[A, B] \equiv AB - BA$ and H is the Hamiltonian of the system. Then the force operator $\mathbf{f}_a$ for the constituent nucleus a may be obtained as

$$\begin{aligned} \mathbf{f}_a &\equiv d\mathbf{P}_a/dt \\ &= i[H, -i(\partial/\partial \mathbf{R}_a)] \\ &= -\partial H/\partial \mathbf{R}_a \end{aligned} \tag{2}$$

where $\mathbf{P}_a$ $(= -i\partial/\partial \mathbf{R}_a)$ and $\mathbf{R}_a$ mean the momentum and position vectors of the nucleus a, respectively. The electrostatic HF theorem (Hellmann, 1937; Feynman, 1939) which states

$$-\partial U/\partial \mathbf{R}_a = \langle -\partial H/\partial \mathbf{R}_a \rangle \tag{3a}$$

is understood as having the force and the negative of the energy gradient equal even in the quantum-mechanical system under the fixed-nuclei approximation. Equation (3a) is a special case of the generalized HF theorem.

In general, the HF theorem (Epstein, 1974, 1981b, and references therein) states that for a given Hamiltonian H, which depends on parameters $\Lambda \equiv \{\Lambda_i\}$, i.e., $H = H(\Lambda)$, with Ψ and U being the corresponding exact normalized eigenfunction and energy eigenvalue, respectively, the following relation holds:

$$\partial U/\partial\Lambda_i = \langle \partial H/\partial\Lambda_i \rangle \equiv \langle \Psi | \partial H/\partial\Lambda_i | \Psi \rangle \tag{3b}$$

The HF theorem is satisfied for a given diatomic molecule at a given internuclear distance, as proved by Hirschfelder and Coulson (1962), if the set of so-called hypervirial relations corresponding to all the parameters $\{\Lambda_i\}$ occurring in H, of the type $\langle [H, W_i] \rangle = 0$ with Hermitian operators $\{W_i\}$, holds. These hypervirial relations are an alternative expression of the floating or stable condition, which will be discussed later. As expected from this viewpoint, the virial and HF theorems have an intimate relation (Frost and Lykos, 1956).

Now, for diatomic systems with the Coulombic potential energy operator

$$\begin{aligned} V = &- \sum_{i=1}^{N} [Z_a/|\mathbf{r}_i - \mathbf{R}_a| + Z_b/|\mathbf{r}_i - \mathbf{R}_b|] \\ &+ \sum_{i>j=1}^{N} 1/|\mathbf{r}_i - \mathbf{r}_j| + Z_a Z_b/|\mathbf{R}_b - \mathbf{R}_a| \end{aligned} \tag{4}$$

the operator $\mathbf{f}_a$ becomes

$$\mathbf{f}_a = -\sum_{i=1}^{N} Z_a(\mathbf{r}_i - \mathbf{R}_a)/|\mathbf{r}_i - \mathbf{R}_a|^3 + Z_a Z_b(\mathbf{R}_b - \mathbf{R}_a)/|\mathbf{R}_b - \mathbf{R}_a|^3 \tag{5}$$

and the force acting on the nucleus a is given by

$$\begin{aligned} \mathbf{F}_a &= \langle \mathbf{f}_a \rangle \\ &= -Z_a \int d\mathbf{r}[(\mathbf{r} - \mathbf{R}_a)/|\mathbf{r} - \mathbf{R}_a|^3]\rho(\mathbf{r}) + Z_a Z_b \mathbf{R}/R^3 \end{aligned} \tag{6}$$

where $\mathbf{R} = \mathbf{R}_b - \mathbf{R}_a$, $R = |\mathbf{R}|$, and $\rho(\mathbf{r})$ is the electron density in position space (cf. Section IX). If we take the $\mathfrak{z}$ axis along the internuclear vector $\mathbf{R}$, only the $\mathfrak{z}$ component of Eq. (6) remains,

$$\begin{aligned} F_a &= (\mathbf{F}_a)_z \\ &= -Z_a \int d[(\mathfrak{z} - \mathfrak{Z}_a)/|\mathbf{r} - \mathbf{R}_a|^3]\rho(\mathbf{r}) + Z_a Z_b/R^2 \end{aligned} \tag{7}$$

since the $\mathfrak{x}$ and $\mathfrak{y}$ components of the force vanish from the symmetry of diatomic systems. Similar discussion holds for the force exerted on the counterpart nucleus b.

Equation (6) or (7) permits an intuitive semiclassical understanding of the quantum-mechanical force; i.e., the force on a nucleus is simply the sum of the electrostatic attraction due to the surrounding electron density $\rho(\mathbf{r})$ and the repulsion due to another nucleus. Thus the HF theorem relates in a rigorous manner the force with the three-dimensional electron density distribution, which guarantees a simpler interpretation of the origin of diatomic interactions when compared with the multidimensional nature of the wave function. [Moreover, we note that the theorem of Hohenberg and Kohn (1964) proves the existence of a unique functional relationship between the electron density and the total energy of a system in its ground state.]

Since the electron density $\rho(\mathbf{r})$ is only the required quantity for the calculation of the force, a decomposition of the density in some manner results in the corresponding decomposition of the electronic force [i.e., the first term of Eq. (7)]. Within the independent-particle model (e.g., Hartree–Fock theory), the force is the sum of orbital contributions. For LCAO–MO wave functions, Bader and co-workers (Bader, 1963, 1981; Bader *et al.*, 1967a,b; Bader and Jones, 1961; Bader and Henneker, 1965; Bader and Bandrauk, 1968a; Cade *et al.*, 1969, 1971) proposed and examined a further partitioning of the orbital force acting on the nucleus *a* into the atomic force due to the one-center atomic density around *a*, the overlap force due to the two-center overlap density, and the screening force which exerts on nucleus *a* by the atomic density centered on nucleus *a* (see Section VII,B). In the electrostatic force theory (Nakatsuji, 1973a–c, 1974a,b; Nakatsuji and Koga, 1974, 1981; Nakatsuji *et al.*, 1973, 1978a–d; Koga *et al.*, 1980a), Nakatsuji proposed a slightly different partitioning into the atomic dipole, exchange, and extended gross charge forces. The atomic dipole force is equivalent to the atomic force due to Bader, but the exchange force represents the net force due to the density in the overlap region which is obtained by subtracting the shielding effect of the two-center density from Bader's overlap force. The rest, including the nuclear repulsion, is the extended gross charge force and represents the force due to the shielded nucleus. Based on Ruedenberg's interference partitioning of electron density (Ruedenberg, 1962), Nakatsuji (1974a) showed that the atomic dipole, exchange, and extended gross charge forces are, respectively, equivalent to the intraatomic interference, interatomic interference, and quasi-classical forces. Nakatsuji's partitioning of the HF force has been shown to be very useful in understanding and predicting various nuclear rearrangement problems such as molecular geometries (Nakatsuji, 1973a–c, 1974a,b; Nakatsuji *et al.*, 1973, 1978a,c,d), chemical reactions (Nakatsuji *et al.*, 1973, 1978b; Koga *et al.*, 1980a), and long-range forces (Nakatsuji and Koga, 1974). In the above two partitionings, however, the problem of basis-set dependence may remain as in the Mulliken population analysis. It is also possible to separate the electronic force based on a spatial or regional partitioning of the density distribution. Berlin's binding–antibinding forces (Berlin, 1951) and their generalization to polyatomic systems (Koga *et al.*, 1978) are examples of such a method, and will be reviewed in Section VII,D in some detail.

Despite the outstanding simplicity and visuality of the force concept, the validity of the HF theorem, Eq. (3), requires some condition when approximate electron densities are employed. The condition is that the parent wave functions must be stable (Hall, 1961) or floating (Hurley, 1954a,b, 1964, 1976; Coulson and Hurley, 1962; Nakatsuji *et al.*, 1978a,c,d; Koga *et al.*, 1980a). [However, there exists in the literature another definition: Wave functions which satisfy the integrated HF theorem are called floating functions (Hurley, 1964; Epstein *et al.*, 1967). At the same time, wave functions satisfying the integral HF theorem are defined as superfloating functions. Superfloating functions are floating, but the converse is not true in general (Epstein *et al.*, 1967).] Hurley (Hurley, 1954a,b, 1964, 1976; Coulson and Hurley, 1962) showed that the HF theorem is satisfied by the wave function composed of floating AOs, whose centers are variationally determined. Nakatsuji (Nakatsuji *et al.*, 1978c) proved that for the force on nucleus a, the HF theorem is satisfied if the AO's belonging to the atom a are floating. Recently, he also showed (Nakatsuji *et al.*, 1980, 1981) that a sufficient condition for the HF theorem is that the basis set includes the derivative AO, $\partial\chi_r/\partial\mathbf{R}'_r$ for any basis χ_r whose center is located at $\mathbf{R}'_r$ (see also, Habiz and Votava, 1980; Nakatsuji *et al.*, 1982, 1983).

In the following discussion we review the force-theoretical studies on diatomic interactions. For the various aspects and miscellaneous applications of the HF theorem and for the force theories of polyatomic systems, the reader should refer to the existing textbooks and reviews (Epstein, 1974; Hurley, 1976; Salem, 1963a; Pimentel and Spratley, 1969; Pilar, 1968; Chandra, 1974; Levine, 1974; Steiner, 1976; Bader, 1970, 1975; Goodisman, 1973; Mulliken and Ermler, 1977; Deb, 1973, 1981; Bamzai and Deb, 1981).

B. Force Analysis of Diatomic Bonding

The nature of chemical bonding in diatomic molecules was extensively studied by Bader and co-workers (Bader, 1963, 1981; Bader *et al.*, 1967a,b; Bader and Jones, 1961; Bader and Henneker, 1965; Bader and

Bandrauk, 1968a; Bader and Nguyen-Dang, 1981; Cade *et al.*, 1969, 1971) based on the forces acting on the nuclei and the distribution of molecular electron density obtained from accurate Hartree–Fock wave functions.

Bader *et al.* first clarified the molecular topography of density distributions. For example, they defined the width and length of a molecule in terms of the density contours of 0.002 a.u. The density difference maps

$$\Delta\rho(\mathbf{r}) \equiv \rho_{\text{molecule}}(\mathbf{r}) - \sum \rho_{\text{atom}}(\mathbf{r}) \tag{8}$$

have been fully utilized and several characteristics have been discussed on the density reorganization upon molecular formations. It has been pointed out that both the amount of charge and the disposition of the charge are important in understanding the bonding. Relaxation of the density distributions has been also discussed with respect to vibrational displacement of nuclei (Bader and Bandrauk, 1968b; Bader *et al.*, 1968; Bader and Ginsberg, 1969).

Subsequently, these density behaviors were rigorously interpreted through the forces exerted on the nuclei. Bader rewrote Eq. (7) as

$$F_a = (Z_a/R^2)[Z_b - \sum_i F_{a,i}] \tag{9}$$

where

$$F_{a,i} = R^2 \int d\mathbf{r}[(z - Z_a)/|\mathbf{r} - \mathbf{R}_a|^3]\rho_i(\mathbf{r}) \tag{10}$$

and $\rho_i(\mathbf{r})$ is the electron density from the ith orbital. $F_{a,i}$ is referred to as charge-equivalent force and is a measure of the degree of the attractive or repulsive contributions to F_a from electrons in the ith MO. Based on the analysis of the $F_{a,i}$ value, Bader *et al.* proposed a classification (for the homonuclear case)

$$F_{a,i} \quad \begin{cases} >1 & \cdots \text{ binding orbital} \\ \sim 1 & \cdots \text{ nonbinding orbital} \\ <1 & \cdots \text{ antibinding orbital} \end{cases} \tag{11}$$

which should be compared with the usual concept of bonding, nonbonding, and antibonding orbitals defined from the orbital energies ε_i. [Note that the $F_{a,i}$ are additive while the ε_i are not additive. For discussion on the binding and bonding, see Tal and Katriel (1977) and Goscinski and Palma (1977).] Equation (10) was further decomposed as

$$F_{a,i} = R^2[F_{a,i}^{(aa)} + F_{a,i}^{(ab)} + F_{a,i}^{(bb)}] \tag{12}$$

where the three terms in the brackets mean, respectively, the atomic, overlap, and screening forces, which are useful to distinguish the density contributions to the diatomic binding. From the examination of various diatomic molecules, it has been deduced that in a covalent bond, the overlap force due to the shared density is the origin of chemical binding, while in an ionic bond, the atomic force on one nucleus or the screening force on the other due to the density migration is significant and the overlap force gives little contribution. In a covalent bond, nuclear descreening occurs because of the distortion of atomic densities and the density accumulation in the overlap region. Then the sum of the atomic and overlap forces gives a measure of the net attractive force, and linear correlation has been found between $\Sigma_i(F_{a,i}^{(aa)} + F_{a,i}^{(ab)})/R_e^2$ and the dissociation energy. [For a more detailed study, see also Hirschfeld and Rzotkierwicz (1974).]

Studies on molecular charge distributions and chemical binding due to Bader and co-workers include the first-row homonuclear diatomics (Bader *et al.*, 1967a), the first-row diatomic hydrides (Bader *et al.*, 1976b), the first-row 12- and 14-electron diatomic series (Bader and Bandrauk, 1968a), the second-row diatomic hydrides (Cade *et al.*, 1969), and the excited, ionized, and electron-attached states of several diatomic molecules (Cade *et al.*, 1971). Bader (1970, 1975, 1981), Deb (1973), and Mulliken and Ermler (1977) review their works in some detail.

Detailed analyses of the density distributions and chemical bindings were also given by Kern and Karplus (1964) for HF and by Ransil and Sinai (1967) for Li_2, N_2, F_2, HF, and LiF. Politzer *et al.* gave a force analysis for CO (Politzer, 1965) and NO (Politzer and Harris, 1970) molecules, and compared (Politzer, 1966) the forces for the H_2 molecule calculated from various wave functions. Clinton and Hamilton (1960) examined force curves for the excited and ionized states of O_2, O_2^+, and NO in relation to the Clinton–Rice reformulation (Clinton and Rice, 1959) of the Jahn–Teller effect (Jahn and Teller, 1937). Curtiss *et al.* (1975) studied ionic binding (see also, Bader and Henneker, 1965) in a series of alkali halides using the density distribution and the Berlin diagram (Berlin, 1951).

C. Force Analysis of Diatomic Interactions

As a natural extension of the force and density study of the diatomic binding problem outlined briefly in the previous discussion, the processes of bond formations have been studied for several diatomic systems as a function of the internuclear separation *R*.

Though the force curves for H_2 and He_2 systems were already examined in 1960 (Bader, 1960a) (see also, Hurley, 1954a,b) as an alternative way to obtain interaction energies, they were only semiquantitative and no detailed analysis was given on the interaction processes. The first

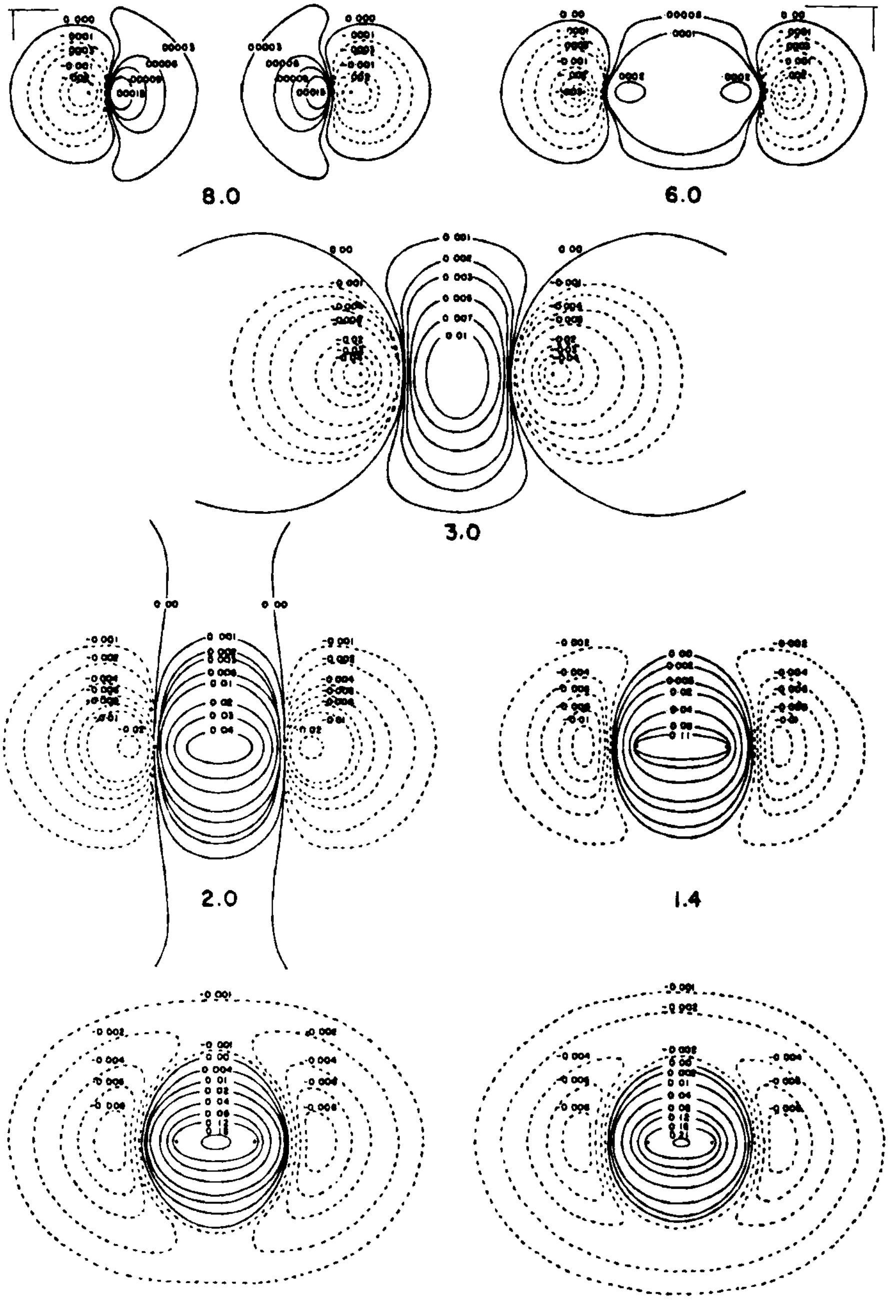


Fig. 5. Density difference contour maps $\Delta\rho$ for the H_2 system at several internuclear distances. The maps for $R = 8.0$ and 6.0 are drawn one-half scale relative to the others. (Reproduced from Bader and Chandra, 1968.)

reliable and detailed study on the diatomic interaction process was reported by Bader and Chandra in 1968. From the force and density point of view, they clarified the origin of the bond formation in H_2 and compared the results with the repulsive interaction in He_2. Figure 5 depicts the density reorganization $\Delta\rho(\mathbf{r})$, and the resultant total force F_a exerted on one of the H nuclei is given in Fig. 6. At a large R (e.g., $R = 8$), the $\Delta\rho$ map shows an inward polarization of the atomic density. The electron density is transformed from the region behind to the region in front of each nucleus. Bader called this a "bootstrap effect" since each nucleus is pulled by its own electron density. The inward polarization at a large separation is the density origin of the so-called London dispersion force (see Section VII,E). The resulting attractive force has its origin in the atomic force. As R decreases, the density accumulation in the overlap region becomes remarkable and the attractive overlap force grows rapidly, which just agrees with the picture of the covalent binding. At $R \sim 5$,

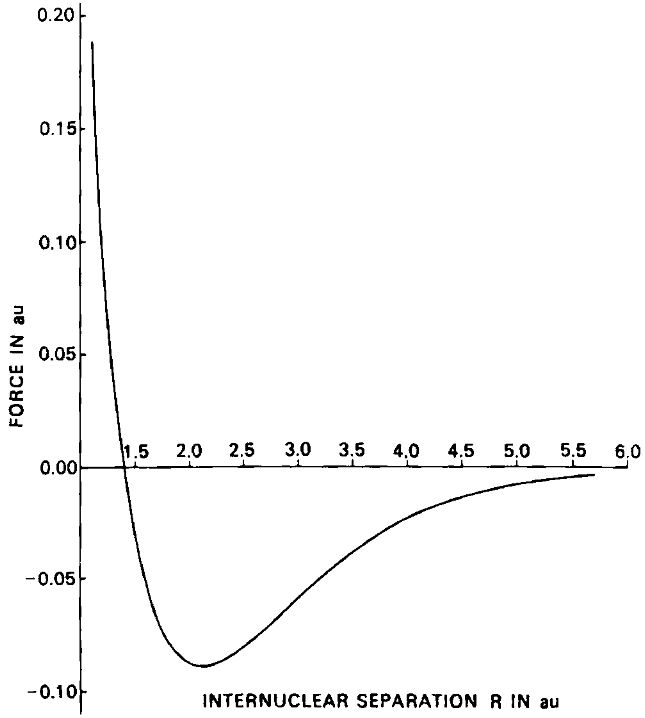


Fig. 6. Force acting on an H nucleus in the H_2 system. Negative and positive values mean attractive and repulsive forces, respectively. (Reproduced from Bader, 1970.)

the contributions of the atomic and overlap forces are comparable and the latter becomes dominant for $5 > R > R_e$. The attraction due to the screening force decreases rapidly for $R < 5$ since the density flows from the atomic to the bond region and since each nucleus penetrates into the density around the other nucleus. The sum of the screening and nuclear forces, which represents the net force by the partially deshielded nucleus, is then repulsive. For a smaller distance $R < R_e$, the charge buildup is also seen in the outsides of the bond region (i.e., antibinding region). The total force is repulsive due to the decreased attraction of the overlap force and the increased repulsion between the deshielded nuclei. The origins for the reaction $H + H \rightarrow H_2$ are thus shown to be an inward polarization of atomic densities in the initial stage and the accumulation of bond density in the intermediate stage. The increased descreening of the nuclear charges works to terminate the reaction at $R = R_e$ in the final stage. These pictures are also valid for polyatomic systems as clarified by Nakatsuji and co-workers (Nakatsuji *et al.*, 1978b; Koga *et al.*, 1980a).

Comparison of these results for the attractive H_2 system with those for the repulsive He_2 system (Figs. 7 and 8) makes the simplicity and visuality of the force treatment more clear. Figure 7 shows the density reorganization approximately reverse to those in the H_2 system. The electron density decreases in the bond region between the two He nuclei and increases in the immediate vicinity of and behind the nuclei. This trend becomes monotonically large as R diminishes. Then the total force given in Fig. 8 is repulsive throughout the process due mainly to the repulsive overlap force, and no stable molecules are formed. The work by Bader and Chandra has well established the advantage of the force analysis of diatomic interactions.

Chandra and Sundar (Chandra and Sundar, 1971; Sundar and Chandra, 1974) carried out a similar analysis for the process $2Li \rightarrow Li_2$. They found that the core density always gives a repulsive force and the binding force of this system comes wholly from the valence density. This is consistent with the large equilibrium bond length and the diffuse density distribution of this molecule. Chandra and Sebastian further examined the interaction processes in He_2^{2+} (Chandra and Sebastian, 1976b), HeH^+ (Chandra and Sebastian, 1976a), He_2^+ (Chandra and Sebastian, 1978), and the first excited state of H_2 (Sebastian and Chandra, 1979). In the case of homopolar interactions, the results agree essentially with those of H_2 and He_2 systems as outlined above. A difference is that for He_2^{2+} and He_2^+, small repulsive forces are observed in the initial stages due to the increased nuclear charges. For the heteropolar HeH^+ interaction, Chandra and Sebastian (1976a) summarized the results as follows: When H^+ ap-

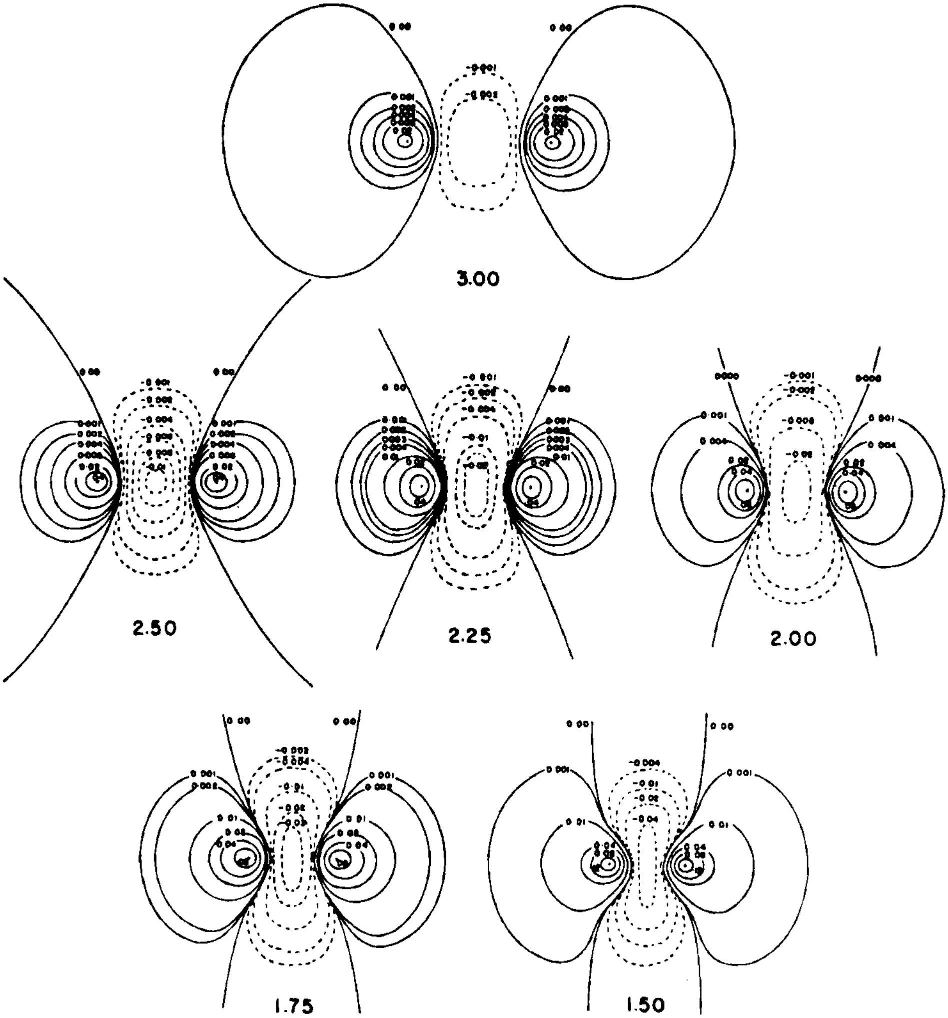


Fig. 7. Density difference contour maps $\Delta\rho$ for the He_2 system at several internuclear distances. (Reproduced from Bader and Chandra, 1968.)

proaches He, the He density is inwardly polarized and transferred into the internuclear region, leading to an attractive force. When He^+ approaches H, the H density is inwardly polarized, but the He^+ density is outwardly polarized. The resultant attraction is small and the equilibrium separation is large in this excited state.

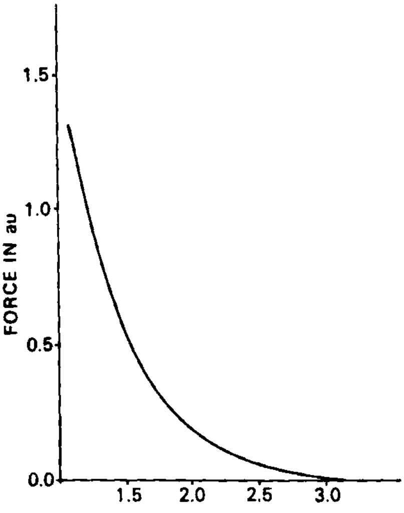


Fig. 8. Force acting on an He nucleus in the He_2 system. Positive value means a repulsive force. (Reproduced from Bader, 1970.)

D. Berlin Diagram and Binding–Antibinding Analysis

Recently, Koga and co-workers (Koga *et al.*, 1980b, 1982a; Koga and Morita, 1980, 1981a) have reported a different analysis of diatomic interactions based on the quantitative application of the Berlin diagram (Berlin, 1951; see also, Koga *et al.*, 1978; Hirschfelder *et al.*, 1964a; Zuvia and Ludeña, 1978).

Berlin (1951) proposed an interesting partitioning of the space of the diatomic density distribution in the following way. Instead of the force on nucleus a, F_a, he considered the force F_R corresponding to the internal coordinate R, which is given by

$$\begin{aligned} F_R &= (1/2)[F_a + F_b] \\ &= -\int d\mathbf{r}\, f_R \rho(\mathbf{r}) + Z_a Z_b / R^2 \qquad (13) \end{aligned}$$

$$f_R = (1/2)[Z_a \cos\theta_a / r_a^2 + Z_b \cos\theta_b / r_b^2] \qquad (14)$$

if the geometric-center-of-the-nuclei coordinates are used. Since $\rho(\mathbf{r})$ is nonnegative, the integrand in the first term of Eq. (13) (i.e., the electronic part) gives attractive contribution if $f_R > 0$, while it gives repulsive contribution if $f_R < 0$. The space of a diatomic system is then separated by the boundary surface $f_R = 0$ into binding ($f_R > 0$) and antibinding ($f_R < 0$) regions (Berlin diagram). The electron density in the binding region gives a binding force which works to pull the two nuclei together, whereas the density in the antibinding region gives an antibinding force which works to push the nuclei apart in cooperation with the nuclear repulsion [the second term of Eq. (13)]. Figure 9 exemplifies this partitioning. The Berlin diagram provides a theoretical definition of "bond region" which is frequently referred to without any specification. However, Berlin's separation into the binding and antibinding regions is not unique and depends on the choice of the coordinate system (Epstein, 1974, 1981b; Koga *et al.*, 1978). Koga *et al.* (1978) have proposed the use of the center-of-mass-of-the-nuclei coordinates and generalized Berlin's idea to polyatomic systems (see also, Johnson, 1974; Bader, 1964; Bader and Preston, 1966). The Berlin diagram has been qualitatively but successfully used to interpret the role of density reorganizations by superposing the diagram on the density difference map (see, for example, Bader *et al.*, 1967a; Koga *et al.*, 1978; Curtiss *et al.*, 1975; Johnson, 1974). Values of the binding and antibinding charges have been examined for some diatomic molecules (Bader *et al.*, 1967a; Bader and Bandrauk, 1968a; Ransil and Sinai, 1967).

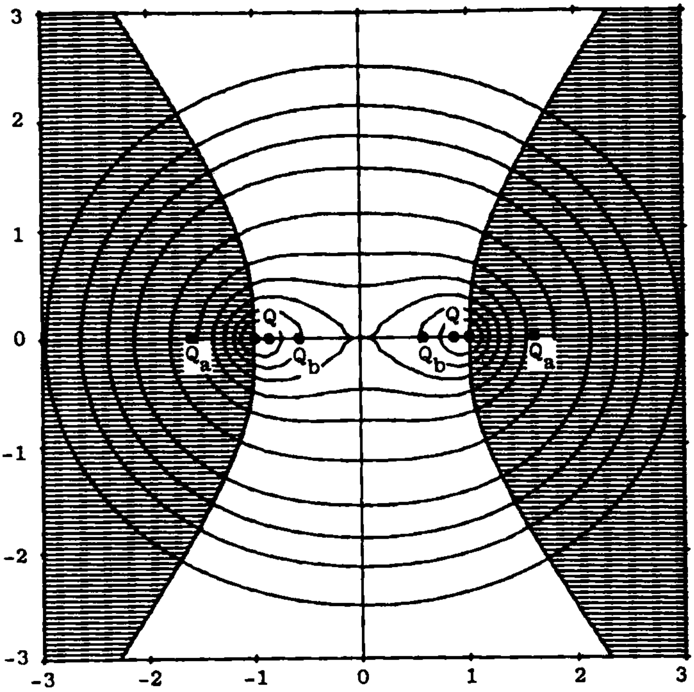
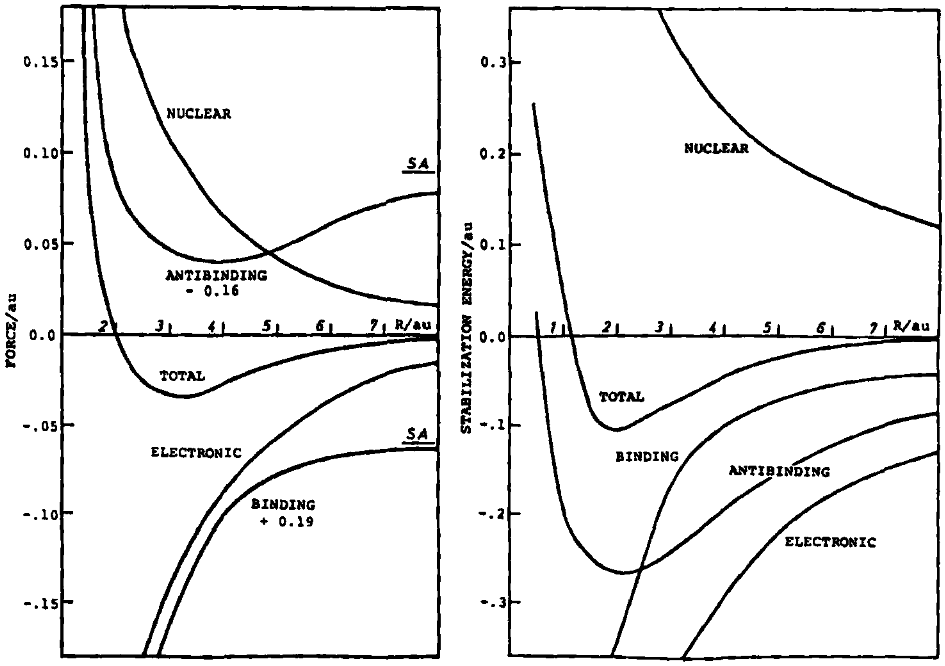


Fig. 9. Berlin diagram superposed on the $1s\sigma_g$ density distribution of the H_2^+ molecule ($R_e = 2.00$). The antibinding regions are shaded. The positions of the total (Q), binding (Q_b), and antibinding (Q_a) CEDs are also given. The contour values are 0.15, 0.125, 0.1, 0.075, 0.05, 0.025, 0.01, 0.005, 0.0025, and 0.001 from the innermost line. (Reproduced from Koga *et al.*, 1982.)

Koga and co-workers (Koga *et al.*, 1980b, 1982a; Koga and Morita, 1980, 1981a) have quantitatively applied the binding–antibinding partitioning to several one-electron diatomic interactions based on the exact wave functions. They examined the partitioning as a function of R for the electronic charge, HF force, and the stabilization energy, which is obtained by integrating the force with respect to R. The center of electron density (CED) has been introduced as a quantitative measure of the density redistribution. For the H_2^+ system, the $1s\sigma_g$, $2p\sigma_u$, $2p\pi_u$, and $3d\pi_g$ states have been examined and compared. The results of the binding–antibinding analysis for the ground $1s\sigma_g$ state are given in Figs. 10 and 11. Of the two components of the electronic force (Fig. 10a), the binding force monotonically increases its attraction from the separated-atom (SA) value and works to stabilize the system (Fig. 10b). The antibinding force decreases its repulsion for R $\gtrsim$ 1.9 (minimum at $R \sim 4.0$) when compared



a b

Fig. 10. The $1s\sigma_g$ state of the H_2^+ system. (a) Partitioning of the HF force. Negative and positive values correspond to attraction and repulsion, respectively. The SA values are −0.25 and 0.25 for the binding and antibinding forces. (b) Partitioning of the stabilization energy. Negative and positive values correspond to stabilization and destabilization, respectively. (Reproduced from Koga *et al.*, 1980.)

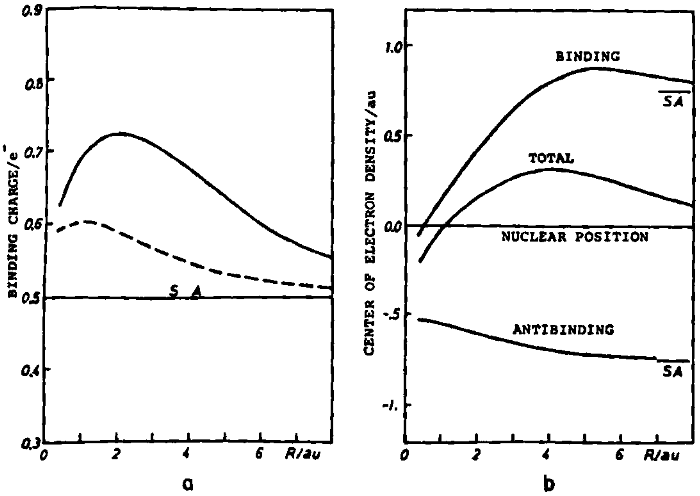
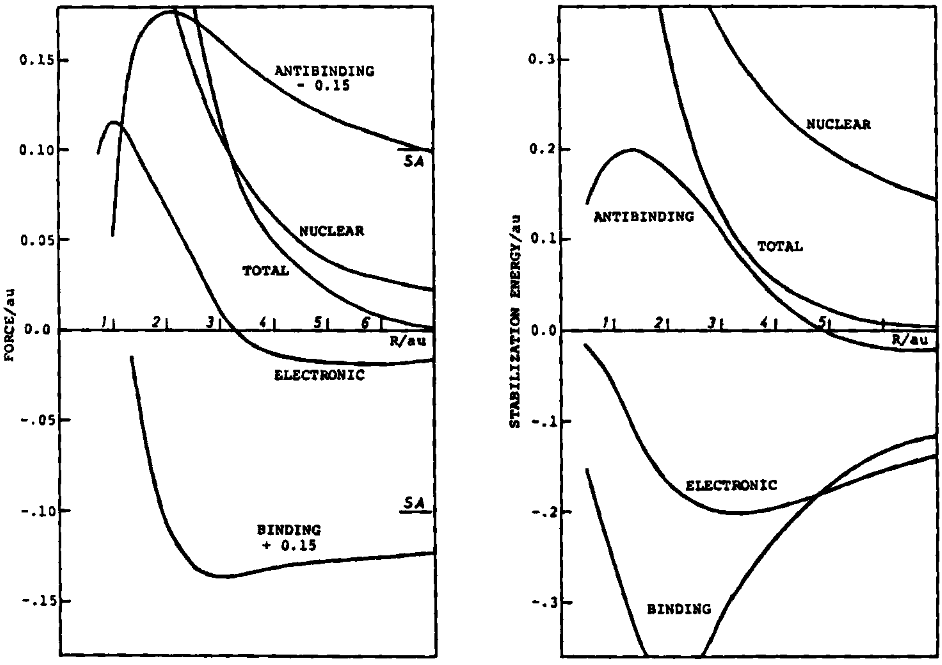


Fig. 11. The $1s\sigma_g$ state of the H_2^+ system. (a) Binding charge. The dashed line shows the binding charge obtained from the superposed atomic density. The SA value is 0.5 e^-. (b) CEDs. Positive value means the inside of the nucleus. The SA values are 0.0, 0.75, and −0.75 for the total, binding, and antibinding CEDs, respectively. (Reproduced from Koga *et al.*, 1980.)

with its SA value. This also contributes to the stabilization. Though both the binding and antibinding parts are cooperative for the bond formation, it is remarkable, as seen in Fig. 10, that the antibinding and total curves are nearly parallel. Figure 10b shows that the antibinding contribution is larger than the binding one for $R \gtrsim 2.5$. The density origin given in Fig. 11 clearly shows the transfer of the electron density from the antibinding to the binding region. At $R_e = 2.00$, the binding charge is 0.72 e^- and it is nearly maximum at this point. All the CEDs shift inward except for the small R range. These density reorganizations are the electron-cloud preceding (Nakatsuji, 1974a,b; Nakatsuji and Koga, 1981), which accelerates the bond formation. As mentioned above, the contributions of the partitioned densities to the force and energy of the system are different, though the amount of the charge decreased in the antibinding region is exactly equal to that increased in the binding region. The analysis of Koga *et al.* suggests that the decrease in the localized antibinding density is more effective for the bond formation than is the increase in the delocalized binding density.

Figures 12 and 13 summarize the results for the antibinding $2p\sigma_u$ state. The increase in the binding force is rather small and the antibinding force increases its repulsion for the R-range of interest. The resultant total force



a b

Fig. 12. The $2p\sigma_u$ state of the H_2^+ system. See legend to Fig. 10. (Reproduced from Koga *et al.*, 1980.)

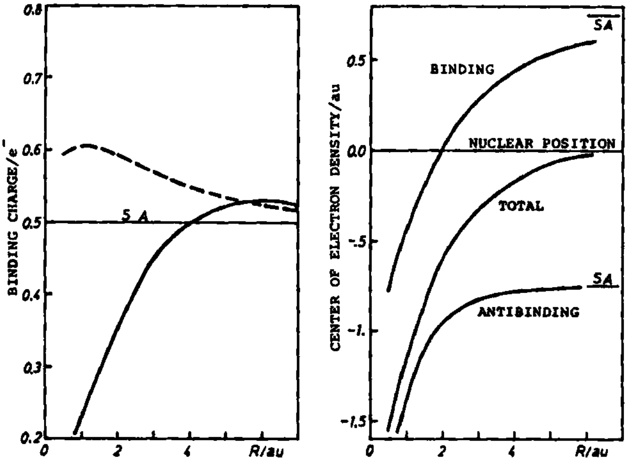


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Fig. 13. The $2p\sigma_u$ state of the H_2^+ system. See legend to Fig. 11. (Reproduced from Koga *et al.*, 1980.)

is repulsive throughout the process. In Fig. 12, the drastic change of the curves for $R < 2$ may be attributed to the united-atom 2pσ(He) character. The repulsion and destabilization in the 2pσ_u state are the result of the electron-cloud following (Nakatsuji, 1974a,b; Nakatsuji and Koga, 1981). Contrary to the electron-cloud preceding observed in the 1sσ_g state, it appears as the transfer of the electron density from the binding to the antibinding region and as the outward shifts of CEDs (Fig. 13). (Note, however, that there is a small increase of the binding charge at a larger R even in the repulsive state.)

For the π states, essential features are common to the σ states. However, since the π densities are delocalized and distribute away from the molecular axis, the results for the π states show larger density reorganizations and smaller force and energy contributions. At $R = R_e$, for example, the binding charge and force are 0.84 e^- and -0.020 in the 2pπ_u state ($R_e = 8$), which should be compared with the corresponding values 0.72 e^- and -0.495 in the 1sσ_g state ($R_e = 2$).

A similar analysis has been carried out for the 1sσ, 2pσ, and 2pπ states of the heteronuclear HeH^{2+} system (Koga and Morita, 1980), and the results have been compared with those of the homonuclear H_2^+ system. From the force-theoretical point of view, it has been questioned whether the relevant electron density is loosely or tightly bound to the nuclei is important. The effect of coordinate dependence of the Berlin diagram has been discussed quantitatively. The binding–antibinding analysis has also been applied to the hydrogen atom–negative charge system, whose interaction consists of electronic repulsion and nuclear attraction (Koga and Morita, 1981a), and to the one-electron homonuclear system with an arbitrary (nonintegral) nuclear charge (Koga *et al.*, 1982a), which models the shielding effect.

Zuvia and Ludeña (1978) examined Li_2 and F_2 systems based on the binding–antibinding partitioning, but only a few internuclear distances were included. In connection to the Bader definition of binding and antibinding orbitals [see Eq. (11)], they proposed the use of the difference between the binding and antibinding charges as this criterion.

E. Long-Range and van der Waals Forces

Further extension of the internuclear separation reduces the diatomic interaction to the problem of long-range and van der Waals forces, where we can neglect the overlap of AOs on different atoms (i.e., there is no overlap density) and apply the perturbation theory with respect to R^{-1} (see, for example, Hirschfelder *et al.*, 1964a).

In his paper on the electrostatic theorem, Feynman (1939) conjectured that the inward polarization of the atomic densities may be the origin of the attractive van der Waals force proportional to R^{-7}. About 30 years later, Frost (1966) examined the long-range forces of H(1s)–H$^+$ and H(1s)–H(1s) systems from the force viewpoint, but his numerical results were not satisfactory since he employed rather crude wave functions. A similar situation has occurred in the calculation of the exchange force between two He atoms (van der Avoird and Wormer, 1977).

In 1967, Hirschfelder and Eliason (Hirschfelder and Eliason, 1967; Hirschfelder and Meath, 1967) succeeded in a quantitative force analysis of the H(1s)–H(1s) long-range interaction. Based on the first- and second-order perturbation wave functions of this system (Hirschfelder and Löwdin, 1959, 1965), the leading term of the long-range force is written as

$$F_a = R^{-7} \int d\mathbf{r}[\cos \theta_a / r_a^2][\rho_{34}^{(1)}(\mathbf{r}) + \rho_{34}^{(2)}(\mathbf{r})] \tag{15}$$

where $\rho_{34}^{(1)}$ and $\rho_{34}^{(2)}$ are the corrections from the first- and second-order wave functions to the density around the nucleus a. The calculated F_a value is

$$\begin{aligned} F_a &= R^{-7}[2.717 + 36.284] \\ &= 39.001 R^{-7} \end{aligned} \tag{16}$$

and is in satisfactory agreement with the energy gradient $-d(6.49903R^{-6})/dR = 38.99418R^{-7}$. Interestingly, the first-order part contributes only 7%, and 93% of this force comes from the second-order part of the wave function, though the corresponding second-order energy is obtained completely from the first-order wave function. This apparent contradiction will be discussed later. The density origin of the van der Waals force Eq. (16) is depicted in Fig. 14. It clearly shows the inward polarization of the atomic density, which is the long-range limit of Fig. 5. The work of Hirschfelder and Eliason (1967) confirmed the validity of Feynman's conjecture (Feynman, 1939).

A more general discussion was given by Nakatsuji and Koga (1974) for the long-range force between two atoms. Based on the electrostatic force theory (see, e.g., Nakatsuji and Koga, 1981), they showed that the origins of the leading terms of diatomic long-range forces are (1) the atomic dipole force for the neutral atoms belonging to the S state, and (2) the atomic dipole and extended gross charge forces for other cases. They applied the results to H(1s)–H$^+$, H(1s)–H(2pσ), and H(1s)–H(2pπ) systems. The final numerical values agreed excellently with those from the energetic theory. The accompanying physical pictures were very simple, as in the H(1s)–H(1s) system.

Apparent contradiction in the perturbative treatment—that the nth-order perturbation wave function determines the energy up to order

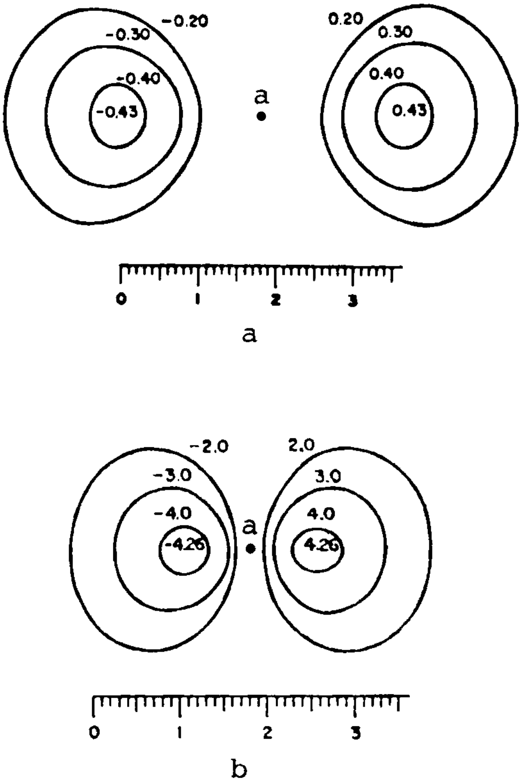

Fig. 14. Contour maps of the second-order perturbation densities in the H(1s)–H(1s) long-range interaction system. Nucleus *b* is located at a large distance *R* to the right. (a) $\rho_{34}^{(1)}$. (b) Effective part of $\rho_{34}^{(2)}$. (Reproduced from Hirschfelder and Eliason, 1967.)

$2n + 1$, while the force, only to order n—was discussed and solved by Steiner (1973) and Koga and Nakatsuji (1976a) (see also Yaris, 1963). They clarified that the use of the relative coordinates which measure the positions of electrons and nuclei from an appropriate point in the interacting subsystem gives the force which correctly corresponds to the perturbation energy. They called such a force a force on whole particles (consisting of electrons and nuclei of each subsystem) and distinguished it from the usual concept of the force on the nucleus obtained in the laboratory-fixed coordinates. The concept of the force on whole particles was exemplified for the calculation of long-range forces in H(1s)–H$^+$, H(1s)–H(1s), and NH$_3$–H$^+$ systems (Koga and Nakatsuji, 1976a). Use of the relative coordinates has been extended for the virial and hypervirial theorems for long-range interactions (Koga and Nakatsuji, 1976b).

VIII. Diatomic Molecular Force Constants

From the point of view of molecular force constants, diatomic molecules generate a class of the simplest systems. Therefore, Stepanov's idea about the transferability of force constants from this simplest class to a more complex one is very fruitful in the study of polyatomic molecules and emphasizes the essential place of diatomics (Stepanov, 1941; Wilson *et al.*, 1955).

In the present section we will discuss the general statements on diatomic force constants, in particular, their definition, general properties, and intercorrelations. However, we do not examine a large variety of computational approaches for obtaining the force constants—they have been presented in detail elsewhere (Rossikhin and Morozov, 1983; Gosteminskaya *et al.*, 1977; Morozov and Bezverkhnaya, 1979; Nielsen, 1951; Sahni *et al.*, 1969; Bezverkhnaya and Morozov, 1980; Pulay, 1969, 1970; Schutte, 1971; Ruttink and van Lenthe, 1981; Mukherjee and McWeeny, 1970). In general, as stated in Section I, we are primarily interested in the "pure" basic principles of the diatomic potential theory.

A. Definitions and General Properties

For the completeness of the context, now we repeat some statements given in Section I.

Definition. Let us consider a given diatomic energy function $U_m(R)$ obtained from quantum-chemical calculations or experimental data, where m enumerates electronic states. We assume that $U_m(R)$ has at least one minimum at $R = R_e$. Then the nth-order diatomic force constant $k_n^{(m)}$ for the mth electronic state is defined as follows:

$$k_n^{(m)} \equiv d^n U_m(R)/dR^n|_{R=R_e}, \qquad n \geq 2 \tag{1}$$

$k_2^{(m)}$ is called the harmonic force constant in common, and others with $n > 2$ are termed anharmonic ones. We notice that (1) in Eq. (1), the differentiation occurs with respect to R alone, and (2) the rigorous and meaningful definition of force constants is valid only in the framework of the adiabatic Born–Oppenheimer approximation.

Let us consider in detail, for example, $k_2^{(0)}$. Applying the second-order perturbation approach to the adiabatic Born–Oppenheimer Hamiltonian, H, of a given diatomic molecule, we obtain the following expressions for $k_2^{(0)}$ (Byers-Brown, 1958; Byers-Brown and Steiner, 1962; Murrell, 1960; Salem, 1963b):

$$k_2^{(0)} \equiv [(\partial^2 V/\partial R^2)_{00} - 2 \sum_{n\neq 0} |(\partial V/\partial R)_{0n}|^2/(U_n - U_0)]_{R=R_e} \tag{2}$$

where $V = V(R)$ is the potential energy part of H and the subscript "00" indicates an average over the ground-state electronic wave function.

The first term in Eq. (2) represents the average value of $\partial^2 V/\partial R^2$, and is equivalent to the classical formula for k_2 and corresponds to nuclear motion with fixed electrons. This quantity is, naturally, positive and quite large (Salem, 1963b). The second term on the right-hand side of Eq. (2) is more complicated and takes into account the effect of the so-called transition force (Byers-Brown, 1958) on the nuclear subsystem, and is due to the change in the charge distribution caused by the nuclear motion. In a particular case of the ground state $[U_n(R) > U_0(R)$ for all $R]$, this term is also large but negative (Salem, 1963b). Therefore $k_2^{(0)}$ is the difference between the two very large terms. It is evident that Eq. (2) is not easy to handle, but Bader (1960b) used it successfully in studying force constants for polyatomic molecules.

One can rewrite Eq. (2) in some equivalent forms (Salem, 1963b; Murrell, 1960):

(a) if Z_A and Z_B are the nuclear z coordinates (Fig. 15):

$$k_2^{(0)} \equiv [(1/2)(\partial^2 V/\partial Z_A^2)_{00} + (1/2)(\partial^2 V/\partial Z_B^2)_{00} - \sum_{n\neq 0} (|(\partial V/\partial Z_A)_{0n}|^2 + |(\partial V/\partial Z_B)_{0n}|^2)/(U_n - U_0)]_{R=R_e} \tag{3}$$

(b) if the midpoint $S = \frac{1}{2}(Z_A + Z_B)$ is fixed:

$$k_2^{(0)} \equiv [(1/4)(\partial^2 V/\partial Z_A^2)_{00} + (1/4)(\partial^2 V/\partial Z_B^2)_{00} - (1/2)(\partial^2 V/\partial Z_A \partial Z_B)_{00} - (1/2) \sum_{n\neq 0} |(\partial V/\partial Z_B)_{0n} - (\partial V/\partial Z_A)_{0n}|^2/(U_n - U_0)]_{R=R_e} \tag{4}$$

(c) and a more elegant expression:

$$k_2^{(0)} \equiv [-(\partial^2 V/\partial Z_A \partial Z_B)_{00} + 2 \sum_{n\neq 0} (\partial V/\partial Z_A)_{0n}(\partial V/\partial Z_B)_{0n}/(U_n - U_0)]_{R=R_e} \tag{5}$$

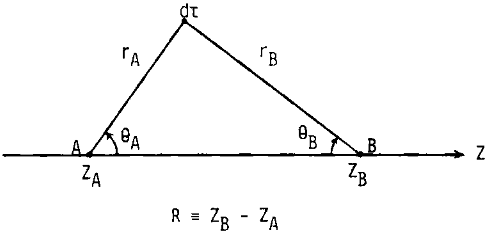

Fig. 15. The coordinate system for diatomic molecules.

At the same time, instead of the V expression, one can transform Eq. (1) for $n = 2$:

$$d^2U/dR^2 = \partial^2U/\partial Z_A^2 = \partial^2U/\partial Z_B^2, \qquad R \equiv Z_B - Z_A \tag{6}$$

$$d^2U/dR^2 = \tfrac{1}{2}(\partial^2U/\partial Z_A^2 + \partial^2U/\partial Z_B^2) \tag{7}$$

$$d^2U/dR^2 = \tfrac{1}{4}(\partial^2U/\partial Z_A^2 - 2\,\partial^2U/\partial Z_A\partial Z_B + \partial^2U/\partial Z_B^2) \tag{8}$$

or finally

$$d^2U/dR^2 = -\partial^2U/\partial Z_A\partial Z_B \tag{9}$$

From the chemical point of view, we must say these equations are not tractable and provide no useful information. In common, the study carried out by many authors (Salem, 1963b; Byers-Brown, 1958; Byers-Brown and Steiner, 1962; Bader, 1960b; Murrell, 1960; Berlin, 1951; Benston and Kirtman, 1966; Davidson, 1962; Benston, 1966; Bader and Bandrauk, 1968b; Kern and Karplus, 1964; Cade *et al.*, 1966; Clinton, 1960; Phillipson, 1963; Empedocles, 1967; Schwendeman, 1966) on the force constants is based on the application of the virial and the Hellmann–Feynman or the electrostatic theorems. In particular, the Hellmann–Feynman theorem provides the expression for k_2 which relates the harmonic force constant to the properties of molecular charge distribution $\rho(\mathbf{r})$, i.e., it follows (Salem, 1963b) that

$$\begin{aligned} k_2^{(0)} = {} & 2Z_AZ_B/R_e^3 \\ & - \Big\{ \int \rho(\mathbf{r})[Z_A(3\cos^2\theta_A - 1)/4r_A^3 + Z_B(3\cos^2\theta_B - 1)/4r_B^3]\,d\mathbf{r} \\ & + (\pi/3)(Z_A\rho_A + Z_B\rho_B) \\ & + (1/2)\int (\partial\rho/\partial Z_B - \partial\rho/\partial Z_A)(Z_A\cos\theta_A/2r_A^2 \\ & + Z_B\cos\theta_B/2r_B^2)\,d\mathbf{r}\Big\}_{R=R_e} \end{aligned} \tag{10}$$

where ρ_A and ρ_B are the electronic charge density at the nuclei A and B, respectively, and the coordinate system is depicted in Fig. 15.

Introducing the field gradients at A and B,

$$g_{A,B} = 2Z_{B,A}/R^3 - \int \rho(\mathbf{r})(3\cos^2\theta_{A,B} - 1)/r_{A,B}^3\,d\mathbf{r} \tag{11}$$

Eq. (10) is transformed to the well-known formula (Salem, 1963b)

$$\begin{aligned} k_2^{(0)} = {} & (1/4)[Z_Ag_A + Z_Bg_B + (4\pi/3)(Z_A\rho_A + Z_B\rho_B) + 4Z_AZ_B/R^3]_{R=R_e} \\ & + (1/2)\Big[\int (\partial\rho/\partial Z_B - \partial\rho/\partial Z_A)(Z_A\cos\theta_A/2r_A^2 \\ & + Z_B\cos\theta_B/2r_B^2)\,d\mathbf{r}\Big]_{R=R_e} \end{aligned} \tag{12}$$

Therefore, the harmonic force constant k_2 is expressed in terms of molecular charge distribution and its variation with R, i.e., we have the expression relating k_2 with the nuclear quadrupole coupling constants obtained experimentally, which is of great importance to the theoretical study of diatomics. Equation (12) is valid not only for exact wave functions but for any functions in which all parameters involved are optimized with respect to R (see Section VII). The Hartree–Fock wave functions belong to this class (Kern and Karplus, 1964; Cade *et al.*, 1966).

In a similar way, all higher order force constants are completely determined, as k_2, by the charge distribution and its higher variations with respect to R.

Bader and Bandrauk (1968b) and, further, Anderson and Parr (1970, 1971) induced a fine structure of the molecular charge distribution introducing the concept of two components of $\rho(\mathrm{r})$, the first part perfectly following the nuclei and the second one being the rest, i.e., nonperfectly following part. This idea is more fruitful because it allows the classical interpretation, and has been developed by many authors (see, for instance, Becker, 1980).

B. Intercorrelations between Force Constants

The first considerable contribution in finding correlations between force constants was made by Varshni (1957). He defined the quantities

$$X \equiv k_3/k_2, \qquad Y \equiv k_4/k_2 \tag{13}$$

and determined the functions

$$F = -[XR_e/3 + 1] \tag{14}$$

$$G = [(5/3)X^2 - Y]R_e^2 \tag{15}$$

as a function of the dimensionless Surtherland parameter $\Delta = k_2R_e^2/2D_e$. He suggested that for 27 diatomics with various natures of bonding, the following equations are satisfied:

$$F = 0.11\Delta + 0.36 \tag{16}$$

$$G = 5\Delta + 9 \tag{17}$$

Though these equations have, of course, the semiempirical nature, they may serve as a basis of constructing the "universal" potential energy function describing diatomic interactions belonging to the same molecular group (Varshni and Majumdar, 1955). Moreover, that F–G-Δ analysis appeared to be very useful for testing potential energy functions (Varshni and Shukla, 1963, 1965).

In order to reproduce the correct diatomic force constants and to find their intercorrelations, it is sufficient to describe adequately the diatomic potential curve near $R = R_e$, because the behavior of the potential curve in that region may suffer little effect from the tail of that curve. In common, the behavior in this intermediate region is well approximated by the Fues diatomic potential function $U_F(R)$ (Fues, 1926; Borkman and Parr, 1968):

$$U_F(R) = U_0 + U_1/R + U_2/R^2 \tag{18}$$

which formally represents the expansion of $U(R)$ in the powers of $1/R$ and takes the first three terms into account. In the case of the Fues potential, cubic and higher order diatomic force constants are expressed in terms of the harmonic force constant (Borkman and Parr, 1968):

$$\begin{aligned} k_3 &= -6k_2/R_e, \qquad & k_4 &= 36k_2/R_e^2 \\ k_5 &= -240k_2/R_e^3, \qquad & k_6 &= 1800k_2/R_e^4, \qquad \text{etc.} \end{aligned} \tag{19}$$

In particular, from Eq. (19), we obtain the following excellent relations (Borkman and Parr, 1968; Parr and Borkman, 1967; Simons and Parr, 1971):

$$(k_2k_4/k_3^2)^{1/2} = 1, \qquad (k_3k_5/k_4^2)^{1/2} = (10/9)^{1/2} \simeq 1 \tag{20}$$

and

$$(k_4k_6/k_5^2)^{1/2} = (9/8)^{1/2} \simeq 1$$

which agree satisfactorily with the experimental results (see Table V).

If we account for the fourth-order term in Eq. (18), the expressions for force constants become as follows (Simons and Parr, 1971; Ohwada, 1982a):

$$k_4 = (36k_2/R_e^2)[1 + (R_ek_3/3k_2)] \tag{21}$$

$$k_5 = -(240k_2/R_e^3)[1 + (R_ek_3/2k_2)] \tag{22}$$

There is no doubt that these modified expressions are, in general, considerably better than Eq. (19). At the same time, in the authors' opinion, one can obtain more accurate results in the Frost–Nalewajski diatomic potential function (see Section VI); at least, this potential predicts diatomic force constants more accurately than any other model diatomic potential functions known in the literature (Nalewajski, 1977). Similar analysis, in particular the test of the validity of Eq. (20), may be carried out for other diatomic functions such as the Morse function (Borkman and Parr, 1968) and the Nalewajski versions of some potential functions (Kryachko, 1983e).

TABLE V

CORRELATIONS BETWEEN DIATOMIC FORCE CONSTANTS[a]

Diatomic molecules	Ratio $(k_2k_4/k_3^2)^{1/2}$	
	Observed	Hartree–Fock
LiH	0.95	0.66
CH	0.92	0.72
OH	1.10	0.75
HF	0.96	0.81
AlH	0.95	0.73
HCl	0.92	0.69

[a] Borkman and Parr (1968).

C. Z-Dependence of Force Constants

There is presently a large volume of literature devoted to the properties of isoelectronic diatomic molecules. Interest in these molecules comes from diverse areas of physics and chemistry. However, most of such literature reports calculations of lifetimes, transition probabilities, and energy levels. To the lesser extent, there have also been calculations and experiments on polarizabilities, NMR chemical shifts, harmonic and higher order force constants, and so on.

It is evident that the physical and chemical properties of diatomic molecules—members of some isoelectronic sequence—change smoothly and systematically with respect to nuclear charge. However, the variability of the nuclear charge must clearly have limits set by the stability of the molecular state. That is, there must exist some values of the nuclear charges which are either too small to bind given atoms together or too large to separate them at some distance. Therefore, there must be some critical values of the nuclear charges.

A considerable contribution to the theoretical study of isoelectronic diatomic molecules was made by Laurenzi (1969, 1972, 1976, 1981), who obtained the equations describing the behavior of R_e, D_e, and k_2 as functions of nuclear charges in both cases of homo- and heteronuclear diatomic molecules. In particular, Laurenzi (1976, 1981) solved exactly these equations for one-electron diatomics with some empirical diatomic potential functions (Morse and Varshni III).

Recently, considerable progress in the study of Z-dependence of diatomic constants was made in papers by March and Parr and co-workers

(March and Parr, 1980; Dreizler and March, 1980; Pucci and March, 1982) and by Ohwada (1982b).

In a particular case of homonuclear neutral diatomic molecules, $1/Z$-expansion of the energy has the following form (March and Parr, 1980):

$$U(Z, R) = Z^{7/3}F_1(Z^{1/3}R) + Z^2F_2(Z^{1/3}R) + Z^{5/3}F_3(Z^{1/3}R) + O(Z^{4/3}) \quad (23)$$

In this expansion, the leading term comes from the Thomas–Fermi theory. At $R = R_e$ the nucleus–electron and electron–electron parts of the energy are as follows:

$$V_{ne}(R_e) = (7/3)Z^{7/3}F_{1e} + 2Z^2F_{2e} + (5/3)Z^{5/3}F_{3e} + (1/3)V_{nn}(R_e) + O(Z^{4/3}) \quad (24)$$

and

$$V_{ee}(R_e) = -(1/3)Z^{7/3}F_{1e} + (1/3)Z^{5/3}F_{3e} + (2/3)V_{nn}(R_e) + O(Z^{4/3}) \quad (25)$$

which provides, as March and Parr (1980) argued, the interpretation of the well-known Teller theorem (Teller, 1962) that states that molecules are not bound in the framework of the Thomas–Fermi theory, because taking a formal limit of $Z \to \infty$, one obtains that the equilibrium bond length R_e becomes infinite, and this in turn means that $V_{nn}(R_e)$ is a term in Z of lower order than $V_{ee}(R_e)$. Regarding this point, further analysis was also done (Dreizler and March, 1980; Pucci and March, 1982, 1983). Ohwada (1982b) obtained the $1/Z$-expansion of $W(R)$ in another way: instead of the March–Parr scaling function (March and Parr, 1980), he based on the Wilson four-dimensional energy density functional (Wilson, 1962) advanced by Parr and Politzer (Politzer and Parr, 1974; Epstein, 1981b) via the Anderson–Parr decomposition of the electron density (Anderson and Parr, 1970).

IX. Momentum-Space Approach to Diatomic Interactions

In classical mechanics, positions and momenta are treated on an equal footing in the Hamiltonian picture. In quantum mechanics, they become operators, but it is true that the position $\mathbf{r}$ and momentum $\mathbf{p}$ of a particle are appropriate conjugate variables that can entirely equivalently describe a state of a system under the commutation relation $[\mathbf{r}, \mathbf{p}] = i$ (Dirac, 1958). This equivalence is usually demonstrated by the example of the one-dimensional harmonic oscillator. The choice of the most appropriate representation depends on convenient description of the phenomenon considered. Generally, the position representation is useful for most bound-state problems such as atomic and molecular electronic structures as well as for many scattering problems. The momentum-space treatment has received little attention in quantum chemistry of atoms and molecules, partly because our everyday intuition is more familiar with the concept of lengths rather than that of velocities and partly because the solution of the integral-type Schrödinger equation in momentum space is not well established.

Some apparent difficulties for the use of the momentum representation may be found in the Coulombic potential operators in momentum space,

$$-Z_A/|\mathbf{r}_i - \mathbf{R}_A| \rightarrow -(Z_A/2\pi^2) \int d\mathbf{p}\, |\mathbf{p}|^{-2} \exp(i\mathbf{p}\mathbf{R}_A) \exp(\mathbf{p}\nabla_{p_i}) \tag{1}$$

for the electron–nucleus attraction potential and

$$+1/|\mathbf{r}_i - \mathbf{r}_j| \rightarrow +(1/2\pi^2) \int d\mathbf{p}\, |\mathbf{p}|^{-2} \exp(\mathbf{p}\nabla_{p_i}) \exp(-\mathbf{p}\nabla_{p_j}) \tag{2}$$

for the electron–electron repulsion potential, where $\exp(\mathbf{p}\nabla_{p_i})$ means the Taylor expansion,

$$\exp(\mathbf{p}\nabla_{p_i})\Psi(\mathbf{p}_1, \ldots, \mathbf{p}_i, \ldots, \mathbf{p}_N) = \Psi(\mathbf{p}_1, \ldots, \mathbf{p} + \mathbf{p}_i, \ldots, \mathbf{p}_N) \tag{3}$$

Indeed, the potential energy operators are rather complicated and their physical pictures are not clear in momentum space. However, we are encouraged by the fact that the kinetic energy operator is transformed as

$$-(1/2)(\partial^2/\partial \mathbf{r}_i^2) \rightarrow +(1/2)|\mathbf{p}_i|^2 \tag{4}$$

and this operator is multiplicative in momentum space. The momentum density $\rho(\mathbf{p})$, the diagonal part of the reduced one-electron density matrix $\gamma(\mathbf{p}, \mathbf{p}')$ in momentum space, is sufficient for the calculation of its expectation value, i.e., the kinetic energy T:

$$T = \int d\mathbf{p}\, (|\mathbf{p}|^2/2)\rho(\mathbf{p}) \tag{5}$$

Equation (4) also implies that the kinetic energy operator is angular independent. Then Eq. (5) is simplified to

$$T = \int_0^\infty dp\, (p^2/2)I(p) \tag{6}$$

where the radial momentum density $I(p)$ is defined by

$$I(p) \equiv \int_0^{2\pi} d\phi_p \int_0^\pi d\theta_p\, p^2 \sin\theta_p \rho(\mathbf{p}) \tag{7}$$

and (p, θ_p, ϕ_p) are the spherical polar coordinates of the momentum vector $\mathbf{p}$. The simplicity of the kinetic energy operator provides a clue for the momentum-space study of diatomic interactions, which is expected to give a new or, at least, complementary development particularly for the density studies of interaction processes, and to serve as a base for the active exploration of the momentum-space approach of the density functional theory (see, for example, Henderson, 1981).

In the following discussion, we shall review the momentum-space aspect of diatomic interactions, focusing upon the redistribution of the momentum density and its contribution to the interaction potential. Since all the readers may not be very familiar with the momentum-space treatment, we start with a brief introduction to the concepts of the momentum wave function and the momentum density.

A. Momentum Wave Function and Momentum Density

The momentum wave function $\Psi(\{\mathbf{p}_i\})$, which constitutes the probability amplitude in momentum space, can be formally obtained by solving the Schrödinger equation in momentum space [for the representation theory, see, Davydov (1965, pp. 85–96), McWeeny (1972, pp. 104–117), Morse and Feshbach (1953, pp. 243–245), and Merzbacher (1961, pp. 135–139)]. Though many developments have been reported for the direct solution of the momentum-space eigenvalue equation (Kaijser and Sabin, 1981; McWeeny and Coulson, 1949; McWeeny, 1949; Lévy, 1950; Fock, 1936; Elsasser, 1933; Svartholm, 1945; Sukumar, 1978; Salpeter, 1951; Salpeter and Goldstein, 1953; Bethe and Salpeter, 1977, pp. 36–47; Shibuya and Wulfman, 1965; Monkhorst and Jesiorski, 1979; Monkhorst and Szalewicz, 1981; Novosadov, 1976, 1979a,b, 1982; Navaza and Tsoucaris, 1981; Lassettre, 1965, 1972, 1973, 1976, 1978, 1981; Huo, 1975, 1977; Huo and Lassettre, 1980; Henderson and Scherr, 1960; Hylleraas, 1932; Bransden and Joachain, 1983, pp. 621–628; Lombardi, 1982), the present status does not yet seem to be at the stage of practical applications to many-electron molecular systems, when compared to the existing methods in position space. The density functional approach in momentum space has been started only recently (Henderson, 1981; Pathak *et al.*, 1982; Gadre and Pathak, 1981).

Alternatively, we can more easily obtain the momentum wave function $\Psi(\{\mathbf{p}_i\})$ from the usual position wave function $\Psi(\{\mathbf{r}_i\})$ by the $3N$-dimensional Fourier transformation (Dirac, 1958),

$$\Psi(\{\mathbf{p}_i\}) = (2\pi)^{-3N/2} \int d\{\mathbf{r}_i\} \exp\left(-i_i \sum_{i=1}^{N} \mathbf{p}_i\mathbf{r}_i\right) \Psi(\{\mathbf{r}_i\}) \tag{8}$$

where N is the number of electrons and $\{\mathbf{p}_i\}$ and $\{\mathbf{r}_i\}$ stand for the sets of electron coordinants in momentum and position spaces, respectively. Due to the isomorphism of the transformation, the Fourier transform of the position wave function composed of LCAO–MOs reduces to the

Fourier transforms of the individual AOs, and hence the momentum representation of various kinds of AOs and their properties have been well studied (Podolsky and Pauling, 1929; Henneker and Cade, 1968; Kaijser and Lindner, 1975; Epstein, 1971; Kaijser and Smith, 1977; Lombardi, 1980, 1982, 1983b; Simas *et al.*, 1982; Komarov and Temkin, 1976; Harmalker *et al.*, 1983; Mukoyama, 1982; Naon *et al.*, 1971; Oddersheda and Sabin, 1982; Yusaf *et al.*, 1980; Gadre *et al.*, 1983; Weniger and Steinborn, 1983; Novosadov, 1983). The Fourier transforms of the Hylleraas-type correlated wave functions for He (Hicks, 1937; Benesch and Thomas, 1979; Zhu *et al.*, 1982; Lombardi, 1983a) and of the exact ellipsoidal wave function for H_2^+ (Glaser and Lassettre, 1966; Thomas, 1972; Liu and Smith, 1978) have also been known.

Here we would like to add some comment of a general character. Dirac (1958) argued that the transformation from classical to quantum mechanics should be made, first by constructing the classical Hamiltonian in the Cartesian coordinate system and then by replacing the positions and momenta by their quantum-mechanical operator equivalents, which are determined by the particular representation chosen. The important point is that this transformation should be performed in the Cartesian coordinate system, for it is only in this system that the Heisenberg uncertainty principle for the positions and momenta is usually enunciated. In this connection, notice that some momentum wave functions such as those obtained by Podolsky and Pauling (1929) are correct wave functions that are useful in calculations of the expectation value of any observable, but at the same time they have a drawback in that the momentum variables used there are not conjugate to any relevant position variables (see also, Lombardi, 1980).

Once the momentum wave function is given, the momentum density $\rho(\mathbf{p})$ and the other reduced density matrices in momentum space are obtained by the same procedure as in position space (Löwdin, 1955; McWeeny, 1960; Davidson, 1976). For example, the momentum density is given by

$$\rho(\mathbf{p}) = N \int d\mathbf{p}_2 \cdots d\mathbf{p}_N |\Psi(\mathbf{p}, \mathbf{p}_2, \ldots, \mathbf{p}_N)|^2 \tag{9}$$

and has the physical interpretation that $\rho(\mathbf{p})\, d\mathbf{p}$ represents the (fractional) number of electrons for finding their momenta within the momentum volume $d\mathbf{p}$ around the point $\mathbf{p}$. The momentum density $\rho(\mathbf{p})$ provides an alternative method of describing the electronic structure of atoms and molecules. Instead of using Eq. (9), we can also obtain the momentum density $\rho(\mathbf{p})$ conveniently from the one-electron density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ in position space (Benesch and Smith, 1970, 1971, 1973; Kaijser and Smith, 1977; Smith, 1982),

$$\rho(\mathbf{p}) = (2\pi)^{-3} \int d\mathbf{r}\, d\,\mathbf{r}' \exp[-i\mathbf{p}(\mathbf{r} - \mathbf{r}')]\gamma(\mathbf{r}, \mathbf{r}') \tag{10}$$

Naturally, the momentum density is a real, positively valued, and inversion-symmetric function (Löwdin, 1967; Kaijser and Smith, 1976a):

$$\rho(\mathbf{p}) = \rho^*(\mathbf{p}) = \rho(-\mathbf{p}) \geq 0 \tag{11}$$

Experimentally, the momentum density is closely connected with the Compton profile, the spectrum of scattered radiation. Within the impulse approximation (Kilby, 1965; Eisenberger and Platzman, 1970), the directional Compton profile is given by

$$J_z(p_z) = \int_{-\infty}^{+\infty} dp_x \int_{-\infty}^{+\infty} dp_y\, \rho(\mathbf{p}) \tag{12}$$

where the p_z axis is chosen parallel to the scattering vector. For isotropic and randomly oriented systems such as gases and liquids, the isotropic Compton profile

$$J(q) = (1/2) \int_{|q|}^{\infty} dp\, p^{-1} I(p) \tag{13}$$

is observed, where the radial momentum density $I(p)$ is given by Eq. (7). For the details, the reader should refer to the recent reviews (Epstein, 1973a, 1975; Williams, 1977a,b; Cooper, 1971, 1977; Aikala, 1977; Bonham *et al.*, 1978; Weyrich, 1975, 1979; Weigold, 1982). It may be noteworthy, however, that in the (e, 2e) experiment we are able to measure not only the total but also the orbital contributions to the Compton profile and the momentum density (McCarthy and Weigold, 1976; Moore *et al.*, 1982).

B. Momentum Distributions of Diatomic Molecules

In the early 1940s, an investigation of chemical bonding from the momentum-space viewpoint was initiated by Coulson and Duncanson (Coulson, 1941a,b; Duncanson, 1941, 1943; Coulson and Duncanson, 1941, 1942; Duncanson and Coulson, 1941) based on the Fourier transformation of the position wave function. [They also gave a systematic analysis of the momentum distributions and the Compton profiles of atoms (Duncanson and Coulson, 1944, 1945, 1948).] They first clarified the momentum-space properties of the fundamental two-center MO and VB wave functions, which may be outlined as follows.

For the single-electron MO function

$$\phi(\mathbf{r}) = (c_a^2 + c_b^2 + 2c_a c_b S)^{-1/2}[c_a\chi_a(\mathbf{r} - \mathbf{R}_a) + c_b\chi_b(\mathbf{r} - \mathbf{R}_b)] \tag{14}$$

with S being the overlap integral, the Fourier transformation gives the momentum wave function

$$\phi(\mathbf{p}) = (c_a^2 + c_b^2 + 2c_ac_bS)^{-1/2} \times [\exp(-i\mathbf{p}\mathbf{R}_a)c_a\chi_a(\mathbf{p}) + \exp(-i\mathbf{p}\mathbf{R}_b)c_b\chi_b(\mathbf{p})] \tag{15}$$

$$\chi_a(\mathbf{p}) = (2\pi)^{-3/2}\int d\mathbf{r}\,\exp(-i\mathbf{p}\mathbf{r})\chi_a(\mathbf{r})$$

The centers of AOs, $\mathbf{R}_a$ and $\mathbf{R}_b$, reduce to the phase factors in momentum space. Then the momentum density is

$$\rho(\mathbf{p}) = (c_a^2 + c_b^2 + 2c_ac_bS)^{-1}\{c_a^2|\chi_a(\mathbf{p})|^2 + c_b^2|\chi_b(\mathbf{p})|^2 + c_ac_b[\exp(-i\mathbf{p}\mathbf{R})\chi_a(\mathbf{p})\chi_b^*(\mathbf{p}) + \exp(+i\mathbf{p}\mathbf{R})\chi_a^*(\mathbf{p})\chi_b(\mathbf{p})]\} \tag{16}$$

where $\mathbf{R} = \mathbf{R}_a - \mathbf{R}_b$ and c_a, c_b, and S are assumed to be real. In the special case of a homopolar bond ($c_a = c_b$ and $\chi_a = \chi_b$), Eq. (16) is simplified to

$$\rho(\mathbf{p}) = (1 + S)^{-1}|\chi_a(\mathbf{p})|^2[1 + \cos(\mathbf{p}\mathbf{R})] \tag{17}$$

It is seen in Eq. (17) that the effect of chemical bonding appears as the oscillation term cos $(\mathbf{pR})$ except for the normalization factor. The momentum density vanishes if $\mathbf{pR} = (2n + 1)\pi$, while it has relative maxima if $\mathbf{pR} = 2n\pi$. Since the oscillation term is always unity in the momentum direction perpendicular to the bond axis, there is a greater probability of finding a given momentum in the perpendicular direction than in the parallel direction. The resultant molecular momentum distribution is an ellipsoid with its minor axis along the parallel axis, which should be compared to spherical distributions for atoms (see Fig. 16 for an example).

In the case of the electron-pair VB function,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = (2 + 2S^2)^{-1/2}[\chi_a(\mathbf{r}_1 - \mathbf{R}_a)\chi_b(\mathbf{r}_2 - \mathbf{R}_b) \times \chi_b(\mathbf{r}_1 - \mathbf{R}_b)\chi_a(\mathbf{r}_2 - \mathbf{R}_a)] \tag{18}$$

the momentum wave function is found to be

$$\psi(\mathbf{p}_1, \mathbf{p}_2) = (2 + 2S^2)^{-1/2}\{\exp[-i(\mathbf{p}_1\mathbf{R}_a + \mathbf{p}_2\mathbf{R}_b)]\chi_a(\mathbf{p}_1)\chi_b(\mathbf{p}_2) + \exp[-i(\mathbf{p}_1\mathbf{R}_b + \mathbf{p}_2\mathbf{R}_a)]\chi_b(\mathbf{p}_1)\chi_a(\mathbf{p}_2)\} \tag{19}$$

and hence the momentum density results in

$$\rho(\mathbf{p}) = (1 + S^2)^{-1}\{|\chi_a(\mathbf{p})|^2 + |\chi_b(\mathbf{p})|^2 + S[\exp(-i\mathbf{p}\mathbf{R})\chi_a^*(\mathbf{p})\chi_b(\mathbf{p}) + \exp(+i\mathbf{p}\mathbf{R})\chi_a(\mathbf{p})\chi_b^*(\mathbf{p})]\} \tag{20}$$

which further simplifies to

$$\rho(\mathbf{p}) = 2(1 + S^2)^{-1}|\chi_a(\mathbf{p})|^2[1 + S\cos(\mathbf{p}\mathbf{R})] \tag{21}$$

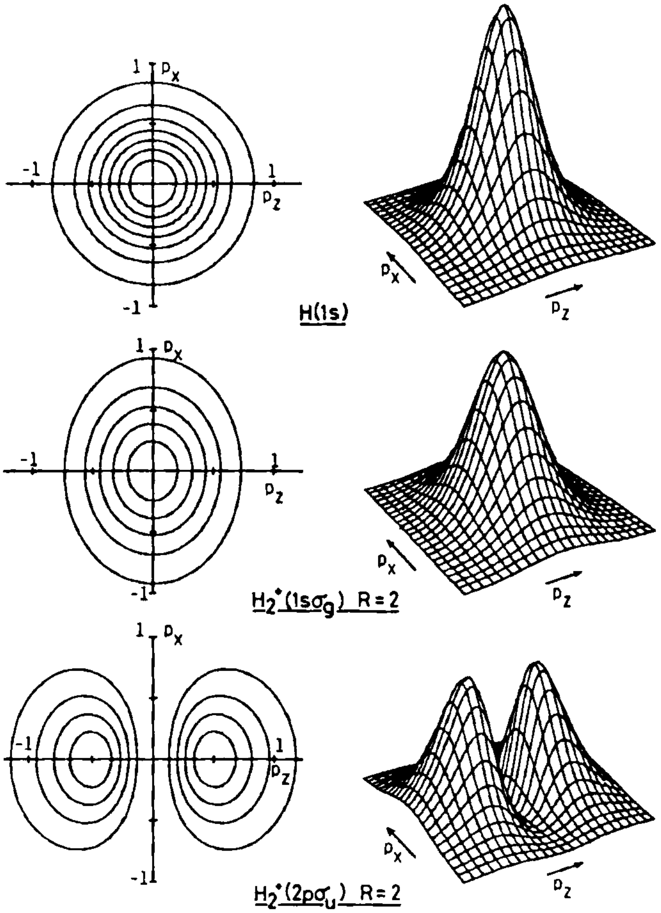

Fig. 16. Typical profiles of momentum density distribution. Contour values are 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 from the outermost line. Perspective plots are drawn in the same scale from the same visual point. All values in atomic units. (Reproduced from Koga and Morita, 1981a.)

when $\chi_a = \chi_b$. In spite of the rather different form of the VB wave function, the momentum density, Eq. (21), is very similar to that of the MO function, Eq. (17), and the oscillating term again plays a predominant role for the bonding effect in momentum space. For the VB function with ionic terms, see Hicks (1937) and Gadre and Narasimhan (1977a). (Note that when we discuss antibonding states, the plus signs in appropriate positions should be replaced with the minus signs in the above equations.)

Subsequently, Coulson and Duncanson applied the results to H_2^+

(Coulson, 1941a; Duncanson, 1941), H_2 (Coulson, 1941a), Li_2 (Duncanson, 1943), N_2 (Duncanson, 1943), and some hydrocarbons (Coulson, 1941b; Coulson and Duncanson, 1941, 1942; Duncanson and Coulson, 1941). Though the wave functions they employed were far less accurate than those available today and their numerical results are only semiquantitative, their studies laid the foundation for the present development of electron theory in momentum space. The pioneer works by Coulson and Duncanson were also reviewed by Sneddon (1951) and Epstein (1977) in some detail.

Recently, more accurate calculations have appeared for the momentum densities and Compton profiles based on the Fourier transforms of the sophisticated position wave functions. Quantitative comparisons have made with the experimental results when available. So far as diatomic molecules are concerned, the following molecules have been theoretically examined in detail: H_2^+ (Thomas, 1972; Liu and Smith, 1978), H_2 (Liu and Smith, 1978; Gadre and Narasimhan, 1977a; Ulsh *et al.*, 1972; Brown and Smith, 1972; Smith *et al.*, 1977; Migdall *et al.*, 1981; Smith, 1977), HeH^+ (Reed and Banyard, 1980), LiH (Ramirez *et al.*, 1977), N_2 (Kaijser and Lindner, 1975; Kaijser *et al.*, 1973, 1980; Cooper and Williams, 1970; Henneker and Cade, 1968; Tawil and Langhoff, 1975; Eisenberger *et al.*, 1972; Kaijser and Smith, 1976b), N_2^+ (Kaijser and Lindner, 1975; Kaijser *et al.*, 1973), O_2 (Langhoff and Tawil, 1975; Tawil and Langhoff, 1975; Eisenberger *et al.*, 1972), F_2 (Snyder and Weber, 1978), CO (Kaijser and Lindner, 1975; Kaijser *et al.*, 1980), CO^+ (Kaijser and Lindner, 1975), NO (Brion *et al.*, 1982), HF (Whangbo *et al.*, 1974; Roux *et al.*, 1967; Cornille *et al.*, 1970), LiF (Henneker and Cade, 1968; Ramirez *et al.*, 1976), NF (Kaijser and Lindner, 1975), NF^+ (Kaijser and Lindner, 1975), HCl (Roux *et al.*, 1967; Cornille *et al.*, 1970), and alkali halides (Ramirez *et al.*, 1976, 1977; Matcha *et al.*, 1978, 1979a,b; Matcha and Pettitt, 1979, 1980; Pettitt *et al.*, 1980). Ramirez (1982, 1983a,b) examined electron momentum distributions of a series of simple diatomic molecules. For the studies of atoms, polyatomic molecules, and solids, and for the experimental results, the reader should consult Epstein (1973a, 1975), Williams (1977a,b), Cooper (1971, 1977), and Weigold (1982). An interesting aspect of polyatomic systems is the transferability and additivity of the Compton profile (Hicks, 1940; Duncanson and Coulson, 1941; Chuang and Hogg, 1967). Particularly, Epstein (Epstein, 1970, 1973a,b, 1975, 1977; Epstein and Lipscomb, 1970) proposed the use of localized MOs, and showed excellent transferability of the momentum density and Compton profile from one molecule to another. [See also Eisenberger and Marra (1971) for the experimental verification.] Based on this additivity, Coulson (1973) then suggested a definition of bond energies from experimental kinetic energies (Epstein, 1973b) through the virial theorem (see, e.g., Slater, 1933).

Though there are many studies on diatomic systems, as briefly summarized above, the subject has been rather limited to the properties of molecules at their equilibrium geometry. Very recently, however, Koga and co-workers (Koga, 1981, 1984b; Koga and Morita, 1981b,c, 1982a; Koga *et al.*, 1982b,c) have proposed a method of momentum density for interatomic interactions, which permits us to investigate the origin and nature of interatomic interactions in terms of the redistribution of the momentum density. We review their works in the next discussion.

C. Momentum Redistributions and Diatomic Interactions

The interaction energy $U(R)$, or, equivalently, the interatomic force $F(R)$ [$\equiv -dU(R)/dR$], is one of the basic properties which characterize diatomic interactions. (R denotes the internuclear distance.) Then the fundamental and important problem is to relate rigorously the momentum density $\rho(\mathbf{p};\, R)$ and its reorganization $\Delta\rho(\mathbf{p};\, R)$ during the interaction process to the energy $U(R)$ and the force $F(R)$ of the system. Focusing on Eqs. (5) and (6), Koga (1981) derived the desired relations and some important guiding principles in the following way. [Though he discussed general relations for polyatomic systems (Koga, 1981; Koga and Morita, 1982a), we outline here only the diatomic case.]

Since the diatomic virial theorem is given by (Slater, 1933)

$$T(R) + U(R) + R[dU(R)/dR] = 0 \tag{22}$$

The energy $U(R)$ can be expressed as a function of the kinetic energy $T(R)$ [compare with Eq. (VI.26)],

$$U(R) = (1/R) \int_R^\infty dR'\, \Delta T(R') - T(\infty) \tag{23}$$

by solving the differential equation, Eq. (22), under the appropriate boundary conditions (Hurley, 1954a, 1962b, 1964; Nalewajski, 1978b,c), where

$$\Delta T(R) \equiv T(R) - T(\infty) \tag{24}$$

and $T(\infty)$ can be replaced with $-U(\infty)$. We also obtain the corresponding expression for the force,

$$F(R) = (1/R^2)\left\{\int_R^\infty dR'\, \Delta T(R') + R\Delta T(R)\right\} \tag{25}$$

Then inserting Eq. (5) or (6) into Eqs. (23) and (25), we obtain the energy $U(R)$ and the force $F(R)$ as a function of the momentum density $\rho(\mathbf{p};\, R)$

or $I(p; R)$ (see below). Applying the kinetic field normalization condition (Nalewajski, 1978b,c) and the equilibrium condition, Koga also derived two more different sets of the basic equations (Koga, 1981), but we are concerned here with the first set shown above.

In order to derive the basic equations, a somewhat different approach was made by Koga and Morita (1981c) based on the integrated (Wilson, 1962; Frost, 1962; Epstein *et al.*, 1967) and integral (Parr, 1964, 1965; Kim and Parr, 1964; Richardson and Pack, 1964; Epstein *et al.*, 1967) Hellmann–Feynman theorems (see also, Hellmann, 1937, pp. 285–286; Feynman, 1939; Deb, 1973, 1981; Bamzai and Deb, 1981; Goodisman, 1973, Vol. 1, pp. 214–241; Hurley, 1976, pp. 20–23). Choosing the electron mass as a differential parameter, Koga and Morita obtained a rigorous $U - \rho(\mathbf{p})$ relation, which may correspond to the $U - \rho(\mathbf{r})$ relation due to Wilson (1962) and Frost (1962). The fact that the kinetic energy operator is the only mass-dependent expression in the Hamiltonian is utilized. Analyzing the mass-dependence of momentum density, however, they then showed that the result is equivalent to one of the previous formulas (Koga, 1981) deduced from the virial theorem. [In other words, it was shown that the Hellmann–Feynman theorem with respect to the electron mass is identical with the virial theorem for a uniform scaling process (Koga and Morita, 1981c).] When the integral theorem has been applied, the energy has been related to the transition momentum density. Interestingly, their method gives a relation between the isotopic energy change and the nuclear momentum density, when the nuclear mass instead of the electron mass is taken as a parameter (Koga and Morita, 1981c; see also, Koga *et al.*, 1983).

Now, using the momentum density $\rho(\mathbf{p})$, we can rewrite Eqs. (23) and (25) as

$$\begin{aligned} \Delta U(R) &\equiv U(R) - U(\infty) \\ &= \int d\mathbf{p}\, (p^2/2) \Delta\bar{\rho}(\mathbf{p}; R) \qquad (26) \end{aligned}$$

$$F(R) = \int d\mathbf{p}\, (p^2/2) \Delta\tilde{\rho}(\mathbf{p}; R) \qquad (27)$$

where the modified momentum densities $\Delta\bar{\rho}$ and $\Delta\tilde{\rho}$ are defined by

$$\Delta\bar{\rho}(\mathbf{p}; R) \equiv (1/R) \int_R^\infty dR'\, \Delta\rho(\mathbf{p}; R) \qquad (28)$$

$$\Delta\tilde{\rho}(\mathbf{p}; R) \equiv (1/R)[\Delta\bar{\rho}(\mathbf{p}; R) + \Delta\tilde{\rho}(\mathbf{p}; R)] \qquad (29)$$

based on the original difference in the momentum density

$$\Delta\rho(\mathbf{p}; R) \equiv \rho(\mathbf{p}; R) - \rho(\mathbf{p}; \infty) \qquad (30)$$

which governs the kinetic energy change [Eq. (24)] during the interaction,

$$\Delta T(R) = \int d\mathbf{p}\ (p^2/2)\Delta\rho(\mathbf{p}; R) \tag{31}$$

All the three density differences must satisfy

$$\int d\mathbf{p}\ \Delta\rho = \int d\mathbf{p}\ \Delta\bar{\rho} = \int d\mathbf{p}\ \Delta\tilde{\rho} = 0 \tag{32}$$

for a given R in order to conserve the number of electrons.

When compared with Eq. (32), it is found that Eqs. (26), (27), and (31) include the kinetic energy operator ($p^2/2$) as a weighting factor in their integrations. Then we get the following guiding principles for the effect of the density redistributions in momentum space on the kinetic and total energies and the interatomic force of a system (Koga, 1981; Koga and Morita, 1981b):

1. For $\Delta T < 0$, $\Delta\rho$ must contract, while for $\Delta T > 0$, $\Delta\rho$ must expand, where the contraction means an increase of low momentum density with a simultaneous decrease of high momentum density and the expansion means the density reorganization reverse to the contraction.
2. For $\Delta U < 0$ (stabilization), $\Delta\bar{\rho}$ must contract, while for $\Delta U > 0$ (destabilization), $\Delta\bar{\rho}$ must expand. At a stable equilibrium, the contraction should be maximum, whereas at the top of a potential barrier, the expansion should be maximum.
3. For $F < 0$ (attraction), $\Delta\tilde{\rho}$ must contract, while for $F > 0$ (repulsion), $\Delta\tilde{\rho}$ must expand. The critical point of the contraction and expansion of $\Delta\tilde{\rho}$ may correspond to the equilibrium distance R_e where F vanishes.

Furthermore, it has been clarified (Koga, 1981) that the contraction of $\Delta\rho$ (and then negative ΔT) is important for the initiation and acceleration of chemical reactions (bond formations), whereas the expansion (and then positive ΔT) is important for the termination of reactions, and that for a large R, the behaviors of $\Delta\rho$, $\Delta\bar{\rho}$, and $\Delta\tilde{\rho}$ are parallel, while at $R = R_e$, $\Delta\rho$ and $\Delta\bar{\rho}$ may show opposite reorganizations.

In Fig. 17, these redistributions of the momentum densities are summarized for the three typical cases of diatomic interactions (Koga, 1981). In the case of attractive interactions, all the density reorganizations are initially contractions and succeedingly change into expansions in the order $\Delta\rho$, $\Delta\tilde{\rho}$, and $\Delta\bar{\rho}$ (Fig. 17a). For repulsive interactions with no stable molecules, the reorganizations may be expansive throughout the interactions (Fig. 17b). When there is a potential barrier (Fig. 17c), the initial

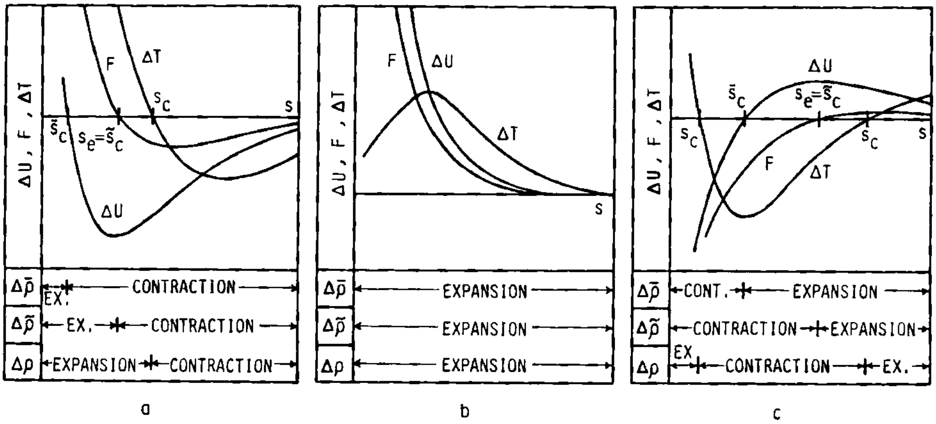

Fig. 17. Schematic representation of curves for energy (ΔU), force (F), kinetic energy (ΔT), and corresponding density reorganizations $\Delta\bar{\rho}(\mathbf{p})$, $\Delta\tilde{\rho}(\mathbf{p})$, and $\Delta\rho(\mathbf{p})$. (a) Attractive interaction with stable equilibrium. (b) Repulsive interaction with no equilibrium. (c) Repulsive interaction with unstable equilibrium. (Reproduced from Koga, 1981.)

expansions and the succeeding contractions will be observed, contrary to the first case.

When we apply Eq. (26), several partitionings of the stabilization energy are possible which seem useful for the analysis of interactions. If we can separate the momentum density into some components, the energy is decomposed into the corresponding components. Within the LCAO formalism, for example, the atom–bond partitioning may be possible based on the one- and two-center parts of the momentum density, though it is basis dependent. The directional partitioning is also possible since the kinetic energy operator ($p^2/2$) is the sum of ($p_x^2/2$), ($p_y^2/2$), and ($p_z^2/2$) (for the details, see Koga, 1981; Koga and Morita, 1981b). The same is true for the kinetic energy, Eq. (31), and the force, Eq. (27).

Note that all the above discussion also holds when we adopt the radial momentum density $I(p)$ or the Compton profile $J(q)$ as a basic physical quantity instead of the three-dimensional density $\rho(\mathbf{p})$ (Koga and Morita, 1981b, 1982a; Thakkar, 1983).

As a simple application of the method outlined above, Koga *et al.* have examined the prototype interactions in the σ ($1s\sigma_g$ and $2p\sigma_u$) and π ($2p\pi_u$ and $3d\pi_g$) states of the H_2^+ system (Koga and Morita, 1981b; Koga *et al.*, 1982b,c). For the σ states, the Finkelstein–Horowitz wave function (Finkelstein and Horowitz, 1928; Coulson, 1937; Dalgarno and Poots, 1953) has been used, which assumes a single hydrogenic 1s orbital for the AOs appearing in Eqs. (14)–(17). Since the momentum representation of the 1s AO is (Podolsky and Pauling, 1929)

$$1\mathrm{s}(\mathbf{p}) = 2^{3/2}\zeta^{5/2}\pi^{-1}(p^2 + \zeta^2)^{-2} \tag{33}$$

the momentum densities $\rho(\mathbf{p})$ and $I(p)$ are found to be

$$\rho(\mathbf{p}) = [2^3\pi^{-2}\zeta^5(1 \pm S)^{-1}](p^2 + \zeta^2)^{-4}[1 \pm \cos(pR\cos\theta_{\mathrm{p}})] \tag{34}$$

and

$$I(p) = [2^5\pi^{-1}\zeta^5(1 \pm S)^{-1}]p^2(p^2 + \zeta^2)^{-4}[1 \pm \sin(pR)/(pR)] \tag{35}$$

where the addition and subtraction represent the bonding $1\mathrm{s}\sigma_{\mathrm{g}}$ and antibonding $2\mathrm{p}\sigma_{\theta}$ states, respectively, and the orbital exponent ζ is variationally optimized at every R. Typical profiles of $\rho(\mathbf{p})$ are shown and compared in Fig. 16 using the contour and perspective plots. The directional Compton profiles required for the parallel–perpendicular partitioning are given by

$$J_{\parallel}(p_{\parallel}) = [2^3 3^{-1}\pi^{-1}\zeta^5(1 \pm S)^{-1}](p_{\parallel}^2 + \zeta^2)^{-3}[1 \pm \cos(p_{\parallel}R)] \tag{36}$$

$$\begin{aligned} J_{\perp}(p_{\perp}) = {} & [3^{-1}\pi^{-1}\zeta^5(1 \pm S)^{-1}]\{2^3(p_{\perp}^2 + \zeta^2)^{-3} \\ & \pm R^3(p_{\perp}^2 + \zeta^2)^{-3/2}K_3(R[p_{\perp}^2 + \zeta^2]^{1/2})\} \end{aligned} \tag{37}$$

where $K_{\nu}(z)$ means the modified Bessel function (Abramowitz and Stegun, 1970; Gradshteyn and Ryzhik, 1980).

In Fig. 18, the three density redistributions, which respectively govern ΔT, ΔU, and F, are given during the $1\mathrm{s}\sigma_{\mathrm{g}}$ interaction process using the radial densities. In Fig. 19, the curves for ΔT, ΔU, and their components obtained from the momentum densities are shown. (The total ΔT and ΔU curves coincide with the results of the direct calculations. The results for F and its components are not given since they agree with the gradients of ΔU and its components.) The ΔI plots show contractions for $R \geq 4$ and expansions for $R \leq 2$, corresponding to the negative and positive ΔT, respectively. The attractive nature of the $1\mathrm{s}\sigma_{\mathrm{g}}$ state is already reflected in these ΔI behaviors. The redistribution $\Delta\bar{I}$ shows contraction whose degree increases with the decrease of R. In accord with the guiding principles, the contraction is maximal at the equilibrium distance $R_{\mathrm{e}} = 2$. At $R = 1$, an expansive character appears for a large momentum region which leads to a positive ΔU. For $R \geq 4$, the difference $\Delta\tilde{I}$ shows contraction corresponding to the attractive force. At $R = R_{\mathrm{e}}$, however, the contractive character is still dominant and the predicted critical nature is not clear. (Finer analysis shows a small expansion for $p > 2.1$, which just balances the contraction.) For $R = 1$, the expansion is observed for $p > 1.1$, and this is the origin of the repulsive force.

The atom–bond partitioning shows a predominant contribution of the atom part in both ΔT and ΔU. This may be attributed to the density flow

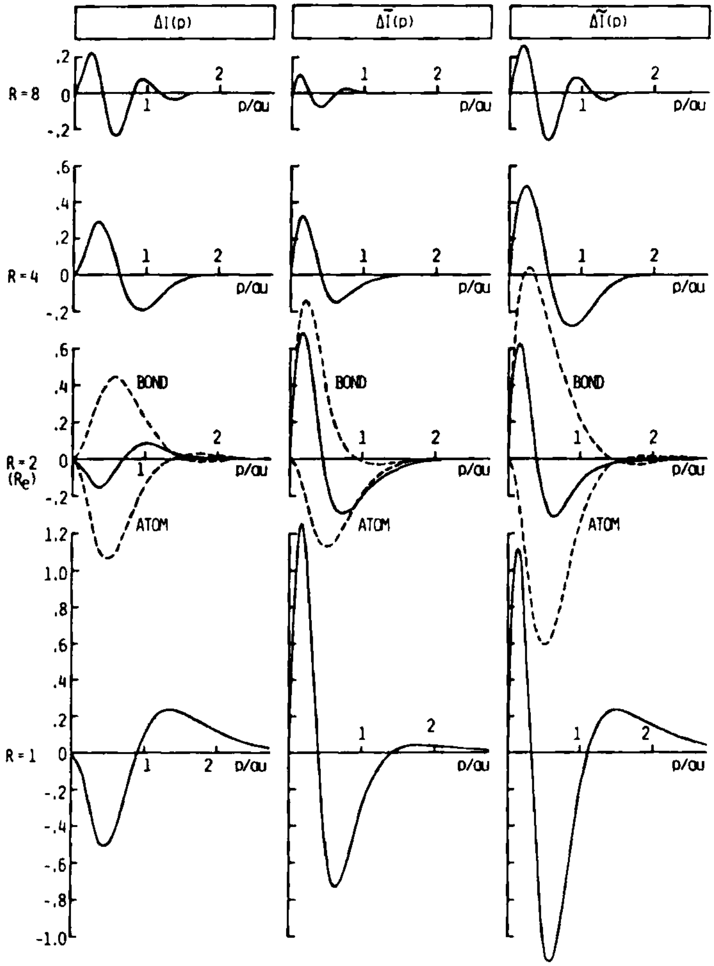

Fig. 18. Differences in the radial momentum densities in the $1s\sigma_g$ state of the H_2^+ system. The ΔI, $\Delta \bar{I}$, and $\Delta \tilde{I}$ govern ΔT, ΔU, and F, respectively. All values in atomic units. (Reproduced from Koga and Morita, 1981a.)

from the atom to the bond part (see the dashed lines in Fig. 18), since this lowers the kinetic pressure, and hence the kinetic and stabilization energies of the atom part. However, the bond part is very important in the final stage, since Fig. 19 shows that the bond part is the origin that makes the ΔU curve turn up for $R < R_e$.

In the directional partitioning, the parallel part contributes predominantly. The significance of this component is in agreement with the results

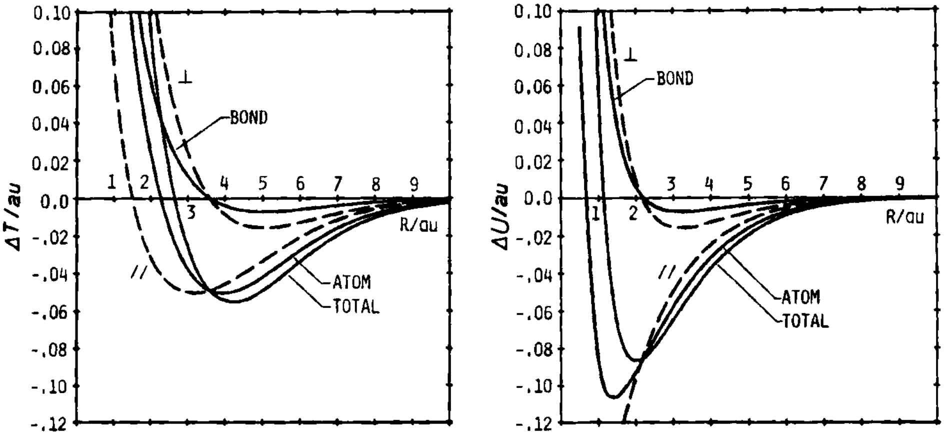

Fig. 19. Kinetic and stabilization energies obtained from the momentum density of the $1s\sigma_g$ state of the H_2^+ system. Their decompositions into the atom–bond and the parallel–perpendicular components are also shown. (Reproduced from Koga and Morita, 1981a.)

of Feinberg and Ruedenberg (Feinberg *et al.*, 1970; Feinberg and Ruedenberg, 1971; Ruedenberg, 1975) and of Hoare and Linnett (1950) that the parallel component of the kinetic energy is most crucial for chemical bonding (see also, Bader and Preston, 1969). As shown in Fig. 20, this is a result of the contraction of the momentum density in this direction, which corresponds to the enlargement of the space of electronic motion from atoms to molecule in position space.

The above discussion for the $1s\sigma_g$ state holds even when a more accurate wave function is employed (Koga *et al.*, 1982b).

The results for the repulsive $2p\sigma_u$ interaction are summarized in Figs. 21 and 22. As the guiding principles predict, all the density redistributions ΔI, $\Delta \bar{I}$, and $\Delta \tilde{I}$ show expansions whose magnitudes increase monotonically with the decrease of R. In the antibonding state, the presence of the nodal plane $p_z = 0$ (see Fig. 16) also works to enhance the expansion. The resultant energy curves again show the predominance of the atom and parallel parts when partitioned.

Similar discussion has been shown also to be valid for the π states (Koga *et al.*, 1982c), and we here omit the detailed review on the π states. A characteristic of π states is that the $\rho(\mathbf{p})$ have sharper and higher peaks near the origin, as compared in Fig. 23. The same trend is observed in $I(p)$ and $J(q)$ depicted in Fig. 24. Thus the π density is more contractive than the σ density in momentum space and the electrons have smaller kinetic energies in π states. Since the momentum and position densities emphasize inverse regions of the respective spaces, the contracted nature of the π momentum density is a direct reflection of the delocalized and diffuse nature of the counterpart position density. Note that, as seen in Fig. 23, the directional character of $\rho(\mathbf{p})$ is the same as that of $\rho(\mathbf{r})$ since the spherical harmonic AO does not change its angular part upon the Fourier transformation (Kaijser and Smith, 1977).

The method of momentum density has also been applied to the long-range force between the ground-state hydrogen atom and the proton (Koga, 1984b), and the results have been compared with those (Nakatsuji and Koga, 1974; see also, Feynman, 1939; Hirschfelder and Eliason, 1967) from the position density based on the electrostatic Hellmann–Feynman theorem (Hellmann, 1937; Feynman, 1939; Deb, 1973, 1981). On the basis of the long-range perturbation theory (Hirschfelder *et al.*, 1964), it has been shown from the momentum-density point of view that

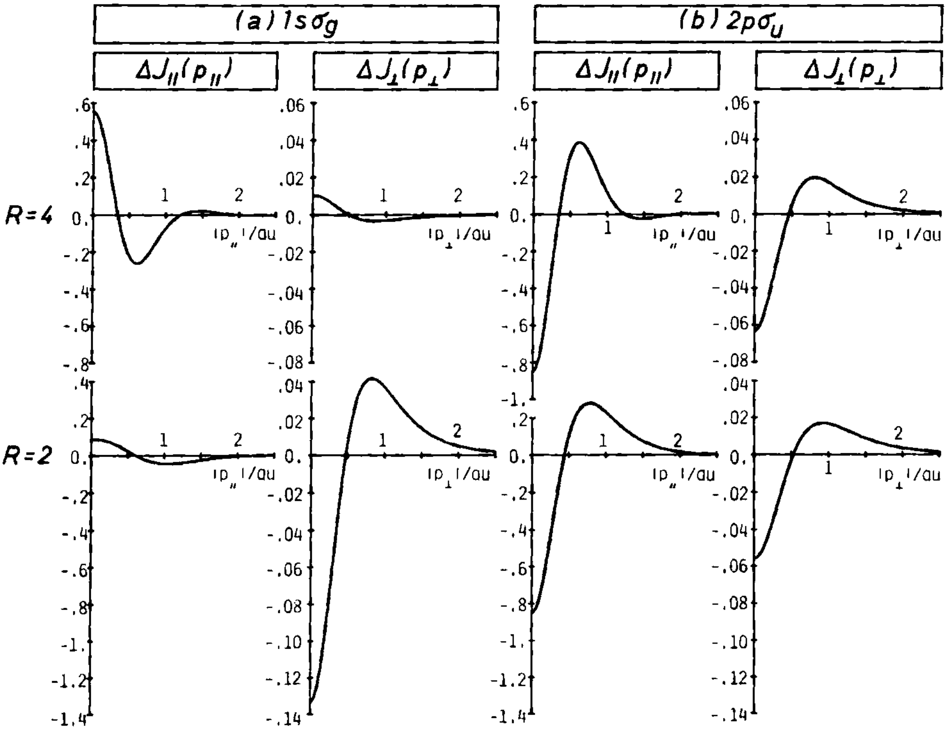

Fig. 20. Differences in the directional Compton profiles for (a) the $1s\sigma_g$ state and (b) the $2p\sigma_u$ state of the H_2^+ system. All values in atomic units. (Reproduced from Koga and Morita, 1981a.)

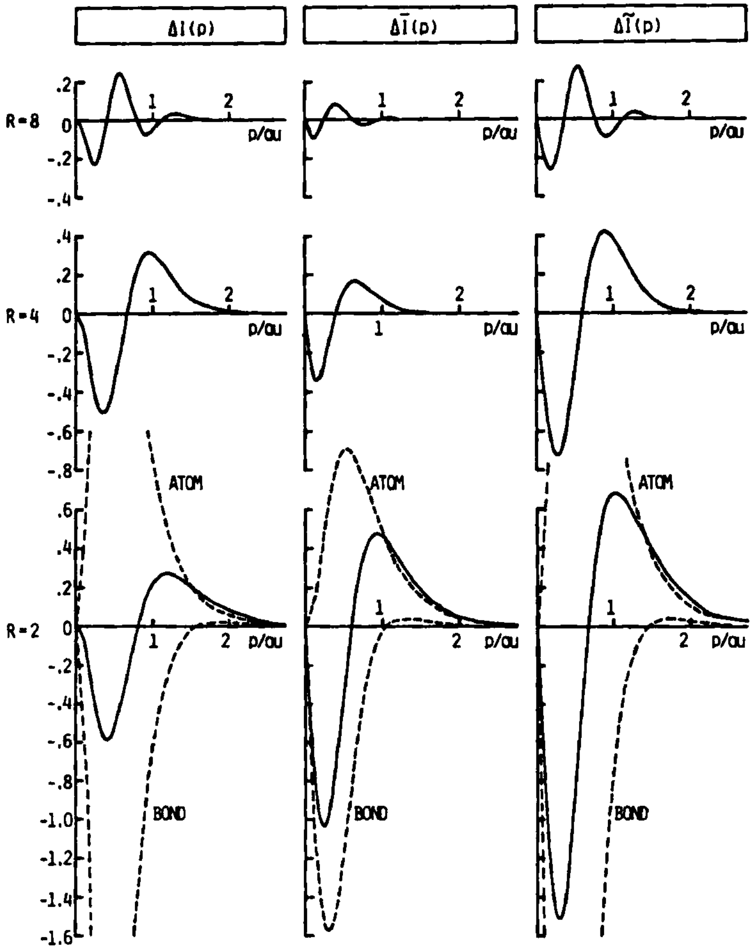

Fig. 21. The $2p\sigma_u$ state of the H_2^+ system. See legend to Fig. 18. (Reproduced from Koga and Morita, 1981a.)

the origin of the second-order stabilization energy $U^{(2)} = -(9/4)R^{-4} + O(R^{-6})$ of this system is the contraction appearing in the second-order momentum density.

The guiding principles of the contraction and expansion for the momentum redistribution have proved valid and common to the various nuclear rearrangement problems thus far examined (Koga, 1981, 1984b; Koga and Morita, 1981b,c, 1982a, 1983; Koga *et al.*, 1982b,c; Thakkar, 1983).

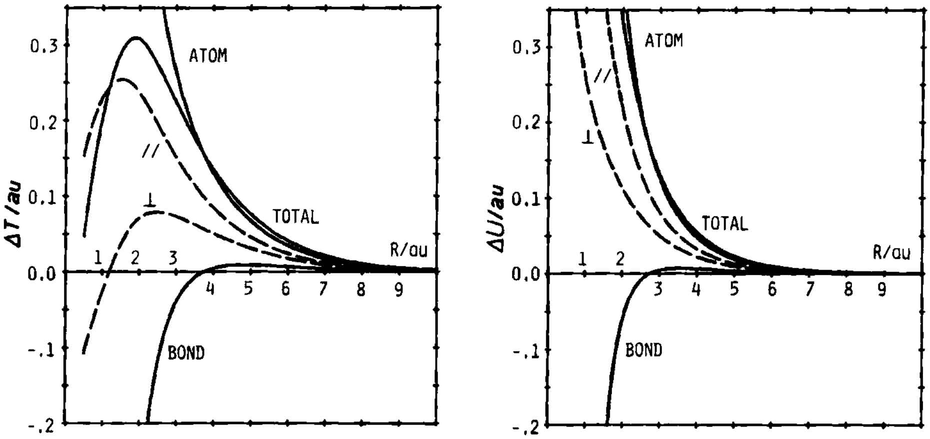

Fig. 22. The $2p\sigma_u$ state of the H_2^+ system. See legend to Fig. 19. (Reproduced from Koga and Morita, 1981a.)

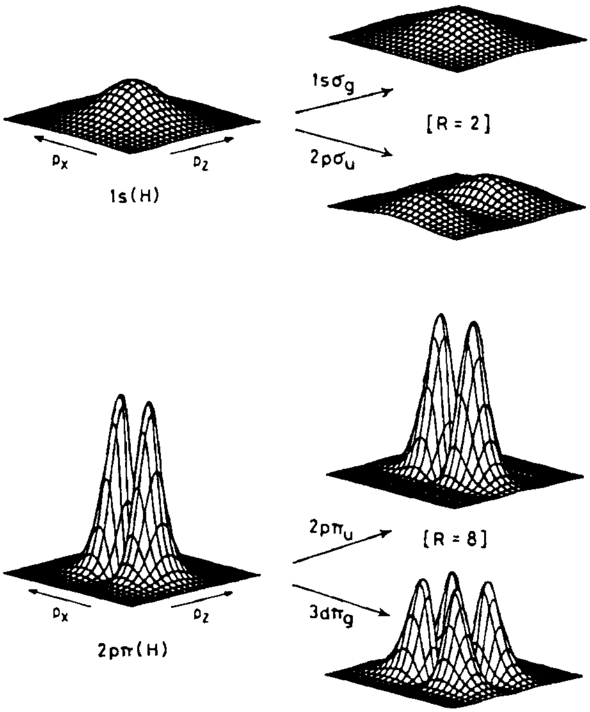

Fig. 23. Perspective plots of electron momentum densities for the σ and π states of the H_2^+ system. These plots are drawn for the region $-1 \leq p_x \leq 1$ and $-1 \leq p_z \leq 1$ in the same scale from the same visual point. All values in atomic units. (Reproduced from Koga *et al.*, 1982.)

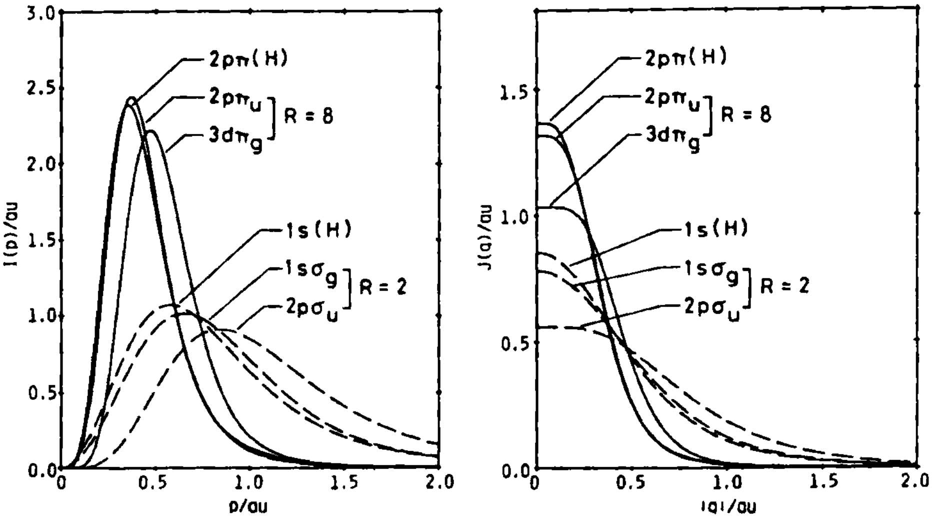

Fig. 24. Radial momentum densities $I(p)$ and isotropic Compton profiles $J(q)$ for the σ and π states of the H_2^+ system. All values in atomic units. [Reproduced from Koga *et al.*, 1982.]

D. Autocorrelation Function and Momentum Expectation Values

The Fourier transform $B(\mathbf{r})$ of the momentum density $\rho(\mathbf{p})$ has been often used to facilitate the analysis and interpretation of experimental Compton profiles (Benesch *et al.*, 1971; Pattison *et al.*, 1981; Kramer *et al.*, 1977; Schülke, 1977; Weyrich *et al.*, 1979; Tossell *et al.*, 1981, 1982; Thakkar *et al.*, 1981) and has been proved to be the autocorrelation function of the position wave function (Benesch *et al.*, 1971; Schülke, 1977). The function $B(\mathbf{r})$ is a clue to bridge the physical pictures in position and momentum spaces and its fundamental properties have been studied in detail by Weyrich *et al.* (1979) and Thakkar *et al.* (1981). Recently, Koga and Morita (1982b) have shown that the various moments $\langle p_x^l p_y^m p_z^n \rangle$ and $\langle p^n \rangle$, which characterize the manner of distribution of the momentum density $\rho(\mathbf{p})$, are immediately obtained from the function $B(\mathbf{r})$. They have applied the results to the H_2^+ interaction and exemplified that insights on the momentum-density redistribution are deduced from the changes of the moments in the course of the interaction (Koga and Morita, 1982b).

The definition and properties of $B(\mathbf{r})$ may be summarized as follows. For simplicity, we treat the spinless one-electron wave function assuming the independent-particle model or the natural orbital expansion (Löwdin, 1955; Benesch and Smith, 1971). Based on the three-dimensional momentum density $\rho(\mathbf{p})$,

$$\rho(\mathbf{p}) = \Psi^*(\mathbf{p})\Psi(\mathbf{p})$$

$$= (2\pi)^{-3} \int d\mathbf{r}\, d\mathbf{r}' \exp(-i\mathbf{p}[\mathbf{r} - \mathbf{r}'])\gamma(\mathbf{r}, \mathbf{r}') \tag{38}$$

the function $B(\mathbf{r})$ is defined as

$$B(\mathbf{r}) = \int d\mathbf{p} \exp(-i\mathbf{p}\mathbf{r})\rho(\mathbf{p}) \tag{39}$$

Then from Eq. (11), $B(\mathbf{r})$ satisfies

$$B(\mathbf{r}) = B^*(\mathbf{r}) = B(-\mathbf{r}) \tag{40}$$

Substituting Eq. (38) for Eq. (39), we obtain

$$B(\mathbf{r}) = \int d\mathbf{r}'\, \gamma(\mathbf{r}', \mathbf{r}' + \mathbf{r}) \tag{41a}$$

$$= \int d\mathbf{r}'\, \Psi^*(\mathbf{r}')\Psi(\mathbf{r}' + \mathbf{r}) \tag{41b}$$

$$= S(\mathbf{r}) \tag{41c}$$

Equation (41a) means that the function $B(\mathbf{r})$ is equivalent to the volume integral of the density matrix $\gamma(\mathbf{r}_1, \mathbf{r}_1')$ under the condition of $\mathbf{r} = \mathbf{r}_1' - \mathbf{r}_1$, and Eq. (41b) means that $B(\mathbf{r})$ is the autocorrelation function of the position wave function $\Psi(\mathbf{r})$. The latter is an application of the Wiener–Khintchin theorem (Jennison, 1961; Bracewell, 1965; Champeney, 1973), which states that the Fourier transform of the power spectrum is equal to the autocorrelation function of a function. Equation (41c) implies not only that $B(\mathbf{r})$ is simply the overlap integral of a wave function with itself separated by the distance $\mathbf{r}$ (Thulstrup, 1976; Weyrich *et al.*, 1979), but also that the momentum density $\rho(\mathbf{p})$ and the overlap integral $S(\mathbf{r})$ are a pair of the Fourier transform. The one-dimensional distribution along the z axis, $B(0, 0, z)$, for example, satisfies

$$B(0, 0, z) = \int_{-\infty}^{+\infty} dp_z \exp(-ip_z z) J_z(p_z) \tag{42}$$

where the directional Compton profile $J_z(p_z)$ is defined by Eq. (12). The radial distribution $\overline{B}(r)$ defined by

$$\overline{B}(r) \equiv \int_0^{2\pi} d\phi \int_0^{\pi} d\theta\, r^2 \sin\theta B(\mathbf{r}) \tag{43}$$

and $I(p)$ given by Eq. (7) are connected by the Hankel transformation (Tossell *et al.*, 1981; Champeney, 1973; Sneddon, 1972)

$$\overline{B}(r) = 4\pi r^2 \int_0^{\infty} dp\, j_0(pr) I(p) \tag{44}$$

where $j_n(z)$ is the spherical Bessel function of the first kind (Abramowitz and Stegun, 1970; Gradshteyn and Ryzhik, 1980).

Since the definition, Eq. (39), means that the $B(\mathbf{r})$ are the characteristic and moment-generating functions of the probability distribution $\rho(\mathbf{p})$, it can be shown (Koga and Morita, 1982b) that

$$\begin{aligned} \langle p_x^1 p_y^m p_z^n \rangle &\equiv \int d\mathbf{p}\, p_x^1 p_y^m p_z^n \rho(\mathbf{p}) \\ &= (i)^{1+m+n} B^{(1,m,n)}(\mathbf{O}) \end{aligned} \tag{45}$$

where $B^{(1,m,n)}(\mathbf{r})$ denotes $\partial^{1+m+n}B(\mathbf{r})/\partial_x^1\, \partial_y^m\, \partial_z^n$, and 1, m, and n are nonnegative integers. Equation (45) implies that various moments $\langle p_x^1 p_y^m p_z^n \rangle$ are, if they exist, immediately obtained from the gradients of $B(\mathbf{r})$ at the origin. The kinetic energy T is, for example, given as the sum of the second gradients of $B(\mathbf{r})$ along the three axes,

$$T = -(1/2)[B^{(2,0,0)}(\mathbf{O}) + B^{(0,2,0)}(\mathbf{O}) + B^{(0,0,2)}(\mathbf{O})] \tag{46}$$

When the moments of one particular component, $\langle p_z^n \rangle$ for instance, are of concern, a similar relation follows from the axial distribution $B(0, 0, z)$. The radial function $\overline{B}(r)$ is useful for the calculation of the moments $\langle p^n \rangle$ where $p = |\mathbf{p}| = (p_x^2 + p_y^2 + p_z^2)^{1/2}$. The result is (Koga and Morita, 1982b)

$$\begin{aligned} \langle p^n \rangle &\equiv \int_0^\infty dp\, p^n I(p) \\ &= \begin{cases} (-1)^{3n/2)}(n+1)b^{(n)}(0) & \text{for even } n \\ (-1)^{(n+1)/2}[2(n+1)/\pi] \int_0^\infty dr\, r^{-1} b^{(n)}(r) & \text{for odd } n \end{cases} \end{aligned} \tag{47}$$

where $b(r)$ is $\overline{B}(r)/(4\pi r^2)$ and $b^{(n)}(r)$ is the nth gradient of $b(r)$. A special case of the kinetic energy is

$$T = -(3/2)b^{(2)}(0) \tag{48}$$

Since $B(\mathbf{r})$ is essentially identical with the overlap integral $S(\mathbf{r})$ [Eq. (41c)], we can obtain various moments of momenta directly from tables of overlap integrals. Note, however, that the moments thus obtained do not always guarantee the existence of those moments.

As an application of the above results, the behaviors of several moments have been examined during the $1s\sigma_g$ bonding process of the H_2^+ system (Koga and Morita, 1982b). Within the Finkelstein–Horowitz approximation, the $B(\mathbf{r})$ function of this system is expressed as (Weyrich *et al.*, 1979)

$$B(\mathbf{r}; \mathbf{R}) = [1 + S(\mathbf{R})]^{-1}\{S(\mathbf{r}) + (1/2)[S(\mathbf{r} + \mathbf{R}) + S(\mathbf{r} + \mathbf{R})]\} \tag{49}$$

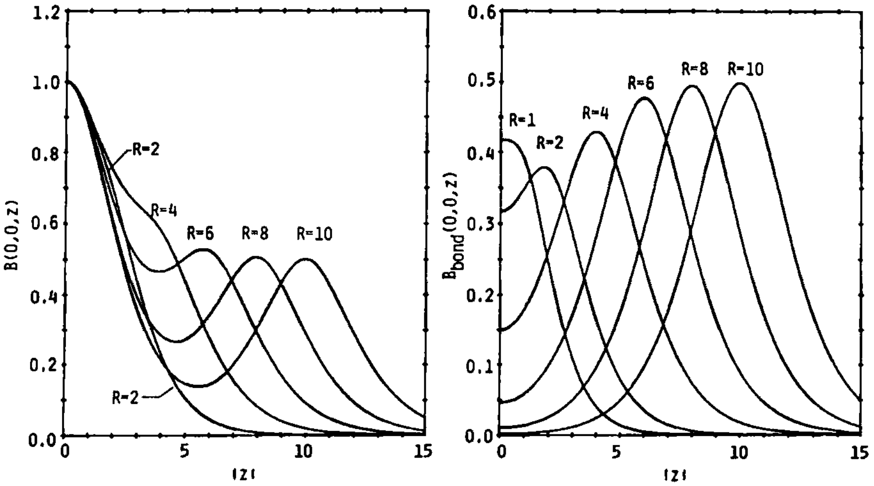

Fig. 25. Changes of $B(0, 0, z)$ and $B_{\mathrm{bond}}(0, 0, z)$ in the $1s\sigma_g$ state of the H_2^+ system.

where $S(\mathbf{r}) = S(|\mathbf{r}|)$ is the overlap integral between the two 1s AOs with exponent ζ. Figure 25 exemplifies the distributions of $B(0, 0, z)$ and its two-center part, $B_{\mathrm{bond}}(0, 0, z)$, where $\mathbf{R}$ is taken to be $(0, 0, R)$. As pointed out by Weyrich *et al.* (1979), $B(0, 0, z)$ shows a secondary peak at $|z| \sim R$ for a large R, due mainly to the nature of $B_{\mathrm{bond}}(0, 0, z)$. By differentiating $B(0, 0, z)$ and $B(x, 0, 0)$, we obtain the second and fourth moments as

$$\begin{aligned}
\langle p_z^2 \rangle &= (1 + S)^{-1}(\zeta^2/3)\{1 + (1 + \zeta R - \zeta^2 R^2)\exp(-\zeta R)\} \\
\langle p_z^4 \rangle &= (1 + S)^{-1}\zeta^4\{1 + [1 - (5/3)\zeta R + (1/3)\zeta^2 R^2]\exp(-\zeta R)\} \\
\langle p_x^2 \rangle &= (1 + S)^{-1}(\zeta^2/3)\{1 + (1 + \zeta R)\exp(-\zeta R)\} \\
\langle p_x^4 \rangle &= (1 + S)^{-1}\zeta^4\{1 + \exp(-\zeta R)\}
\end{aligned} \qquad (50)$$

The changes in these moments from the corresponding values of the hydrogen atom are plotted in Fig. 26. In addition to the previous results (Koga and Morita, 1981b) discussed in Section IX,C, they provide further insight into the reorganization of momentum density during the interaction. Koga and Morita (1982b) gave the following interpretations: (1) Since the behaviors of the fourth moments resemble each other but those of the second moments do not, it is suggested that the anisotropy in the momentum redistribution is dominant in the low momentum region. (2) Since the changes $\Delta\langle p_z^2 \rangle$ and $\Delta\langle p_z^4 \rangle$ have opposite signs for $1.5 \lesssim R \lesssim 3.4$, the contractive and expansive reorganizations, respectively, at the

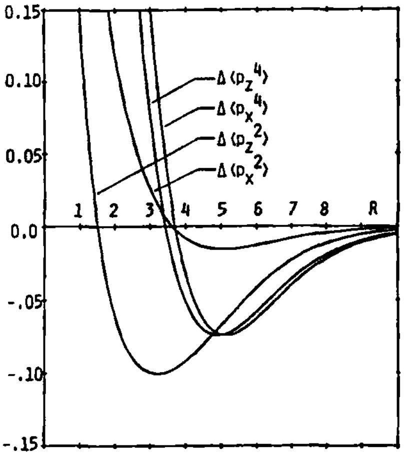

Fig. 26. Changes of the second and fourth moments parallel and perpendicular to the bond axis in the $1s\sigma_g$ state of the H_2^+ system. [Reproduced from Koga and Morita, 1982.]

small and large p_z regions seem to occur simultaneously for this R-range due to the oscillating term $\cos(p_zR)$ [see Eq. (17)]. (3) Among the four moments, $\Delta\langle p_z^2\rangle$ shows the largest change, which is consistent with the significance of the parallel part of the kinetic energy in chemical bonding.

The corresponding relations between the moments $\langle p_x^{-l}p_y^{-m}p_z^{-n}\rangle$ and $\langle p^{-n}\rangle$ and the autocorrelation functions $B(\mathbf{r})$ and $b(r)$ have also been reported very recently (Koga, 1983).

The moments $\langle p^n\rangle$ are important properties by themselves, not only since they characterize the nature of momentum distributions and Compton profiles (as exemplified above), but also since they are related to several physical properties. For example, $\langle p^{-1}\rangle$ is just half the peak height of the isotropic Compton profile $J(0)$. The average momentum of electrons is $\langle p\rangle$ and has been reported (Pathak and Gadre, 1981) to have a good correlation with the Hartree–Fock exchange energy for atoms. Evidently, $\langle p^2\rangle$ is twice the kinetic energy T, which is the negative of the total energy U if the virial theorem holds in its simplest form; $\langle p^4\rangle$ appears in the approximate relativistic correlation to the electronic kinetic energy (Hirschfelder *et al.*, 1964). In this connection, the properties and interrelations of the moments $\langle p^n\rangle$ have been studied extensively (Sears and Gadre, 1981; Gadre and Sears, 1979; Pathak and Gadre, 1981; Gadre and Pathak, 1982; Gadre, 1979; Gadre and Matcha, 1981, 1982; Gadre and Narasimhan, 1976, 1977b, 1978; Gadre *et al.*, 1982; Thakkar, 1982; Thakkar *et al.*, 1980; Epstein and Roux, 1974; Roux, 1978; Dmitrieva and Plindov, 1982, 1983). The moments have been also used to construct approximate Compton profiles and momentum densities (Sears and Gadre, 1981; Gadre and Sears, 1979; Koga and Morita, 1983; Koga, 1984a).

X. Density Functional Representation of Diatomic Interactions

The first statistical models of these interactions are the well-known Thomas–Fermi (TF) and Thomas–Fermi–Dirac (TFD) theories based on the idea of approximating the behavior of electrons by that of the uniform negatively charged gas. Some authors (Sheldon, 1955; Teller, 1962; Balázs, 1967; Firsov, 1953, 1957; Townsend and Handler, 1962; Townsend and Keller, 1963; Goodisman, 1971) proved that these theories provide an adequate description of purely repulsive diatomic interactions. Abrahamson (1963, 1964) and Konowalow *et al.* (Konowalow, 1969; Konowalow and Zakheim, 1972) extended this region to intermediate internuclear distances, but Gombas (1949) and March (1957) showed that the Abrahamson approach is incorrect, and so the question of how adequately the TFD theory provides diatomic interactions for closed-shell atoms is still open. Here we need to note that until recently, there has existed only work by Sheldon (1955), as far as we know, in which the TFD interaction potential is actually calculated by solving the TFD equation for a series of internuclear distances (see also, Kaplan, 1982).

It is well known (Gombas, 1949; March, 1957; Goodisman, 1973) that the TFD theory is based on the minimization of the free-electron gas density energy functional, and as a result we obtain the relations between the electron density at some point of position space and the total electrostatic potential at that point. Combining it with the Poisson equation results in the basic TFD nonlinear differential equation.

The applications of the TFD theory to the study of diatomic interactions are discussed in detail by Goodisman (1973), and here we are concerned only with the recent state of this art. In particular, Yonei and Goodisman (1977) studied Ar–Ar and Ne–Ne diatomic interactions via the TFD theory.

Another approach based on the energy density functional to study diatomic interactions was proposed by Gaydaenko and Nikulin, and Gordon and Kim (Gaydaenko and Nikulin, 1970; Nikulin, 1971; Kim and Gordon, 1974; Clugston and Gordon, 1977; Waldman and Gordon, 1979; Kolos and Radzio, 1978), and is called the Gordon–Kim (GK) approach. In the framework of the GK approach, the interaction between two atoms, A and B, in the system AB is given as follows:

$$\Delta E^{\mathrm{st}}_{\mathrm{int}} = E^{\mathrm{st}}_{\mathrm{AB}} - E^{\mathrm{st}}_{\mathrm{A}} - E^{\mathrm{st}}_{\mathrm{B}} \tag{1}$$

where

$$E^{\mathrm{st}}_{X} = E^{\mathrm{st}}_{X,\mathrm{kin}} + E^{\mathrm{st}}_{X,\mathrm{exch}} + E^{\mathrm{st}}_{X,\mathrm{Coul}} + E^{\mathrm{st}}_{X,\mathrm{corr}} \tag{2}$$

and $E^{\mathrm{st}}_{X,\mathrm{kin}}$, $E^{\mathrm{st}}_{X,\mathrm{exch}}$, $E^{\mathrm{st}}_{X,\mathrm{Coul}}$, and $E^{\mathrm{st}}_{X,\mathrm{corr}}$ denote the kinetic, exchange, Coulomb, and correlation energies for a system (where X = A, B, AB) and are obtained via the statistical theory of matter:

$$E^{\mathrm{st}}_{X,\mathrm{kin}} = (3/10)(3\pi^2)^{2/3} \int [\rho_X(\mathbf{r})]^{5/3}\, d\mathbf{r} \tag{3}$$

$$E^{\mathrm{st}}_{X,\mathrm{exch}} = -(3/4)(3/\pi)^{1/3} \int [\rho_X(\mathbf{r})]^{4/3}\, d\mathbf{r} \tag{4}$$

$$E^{\mathrm{st}}_{X,\mathrm{Coul}} = -Z_X \int \rho_X(\mathbf{r})/|\mathbf{R}_X - \mathbf{r}|\, d\mathbf{r} + \frac{1}{2}\iint \rho_X(\mathbf{r})\rho_X(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|\, d\mathbf{r}\, d\mathbf{r}' \tag{5}$$

$$E^{\mathrm{st}}_{X,\mathrm{corr}} = \int \varepsilon^{\mathrm{st}}_{\mathrm{corr}}[\rho_X(\mathbf{r})]\rho_X(\mathbf{r})\, d\mathbf{r} \tag{6}$$

where Z_X and $\mathbf{R}_X$ denote the charge and radii vector of X, respectively, and $\varepsilon^{\mathrm{st}}_{\mathrm{corr}}[\rho_X(\mathbf{r})]$ is the correlation energy density functional. As evident from Eqs. (1) and (2), the interaction energy $\Delta E^{\mathrm{st}}_{\mathrm{int}}$ obtained via the GK theory consists of the following four contributions:

$$\Delta E^{\mathrm{st}}_{\mathrm{int}} = \Delta E^{\mathrm{st}}_{\mathrm{kin}} + \Delta E^{\mathrm{st}}_{\mathrm{exch}} + \Delta E^{\mathrm{st}}_{\mathrm{Coul}} + \Delta E^{\mathrm{st}}_{\mathrm{corr}} \tag{7}$$

The basic simplification of the Gaydaenko–Nikulin–Gordon–Kim approach consists in the approximation of $\rho_{\mathrm{AB}}(\mathbf{r})$ as a sum of the atomic densities $\rho_{\mathrm{A}}(\mathbf{r})$ and $\rho_{\mathrm{B}}(\mathbf{r})$:

$$\rho_{\mathrm{AB}}(\mathbf{r}) = \rho_{\mathrm{A}}(\mathbf{r}) + \rho_{\mathrm{B}}(\mathbf{r}) \tag{8}$$

Usually, in the framework of this statistical approach, it is suggested that the densities $\rho_{\mathrm{A}}(\mathbf{r})$ and $\rho_{\mathrm{B}}(\mathbf{r})$ are obtained by using the Hartree–Fock wave functions of both atoms, which are available for most neutral atoms and some ions (Clementi, 1965).

Now we discuss the choice of representations for the components of E^{st}_X, and we limit ourselves to the particular case in which X is an atom. First we consider $\varepsilon^{\mathrm{st}}_{\mathrm{corr}}[\rho_X(\mathbf{r})]$. Gordon *et al.* (Gordon and Kim, 1972; Kim and Gordon, 1974) choose $\varepsilon^{\mathrm{st}}_{\mathrm{corr}}$ of the following form (Carr *et al.*, 1961; Carr and Maradudin, 1964) for both high- and low-density regions, interpolating it by a simple logarithm function:

$$\varepsilon^{\mathrm{st}}_{\mathrm{corr}}[\rho_X(\mathbf{r})] = \begin{cases} 0.0311 \ln r_s - 0.048 + 0.009 r_s \ln r_s - 0.01 r_s, & r_s \le 0.7 \quad (9a) \\ -0.06156 + 0.01898 \ln r_s, & 0.7 < r_s < 10 \quad (9b) \\ -0.438 r_s^{-1} + 1.325 r_s^{-3/2} - 1.47 r_s^{-2} - 0.4 r_s^{-5/2}, & r_s \ge 10 \quad (9c) \end{cases}$$

where $r_s = [(3\pi/4)\rho_X(\mathbf{r})]^{1/3}$.

Notice that this expression for the correlation energy density functional is obtainable only in the high- and low-density limits, and one must rely upon an approximate interpolation formula, Eq. (9b), for the intermediate densities, which are the most important regions for atoms and molecules. Notice also that applying this formula to rare gas atoms (Kim and Gordon, 1974), we obtain a correlation energy that is in poor agreement with experiment, roughly a factor of 2 too large. In this connection, satisfactory agreement can be obtained in the framework of the McWeeny approach (McWeeny, 1976), where

$$\varepsilon_{\mathrm{corr}}^{\mathrm{st}} = -\{9.652 + 2.946[\pi_X(\mathbf{r})]^{-1/3}\}^{-1} \tag{10}$$

This result agrees well with the usual expression for high- and low-density regions, Eqs. (9a) and (9c), and it permits the evaluation of the energy density without any interpolation for the intermediate density region. As easily shown, Eq. (10) is comparable with the Wigner formula (Wigner, 1934) for a uniform electron gas. Developing McWeeny's idea, Brual and Rothstein (1978, 1979) suggested $\varepsilon_{\mathrm{corr}}^{\mathrm{st}}[\rho_X(\mathbf{r})]$ in a more general form:

$$\varepsilon_{\mathrm{corr}}^{\mathrm{st}} = -\{\alpha + \beta[\rho_X(\mathbf{r})]^{-1/3}\}^{-1} \tag{11}$$

with $\alpha = 9.810$ and $\beta = 21.437$, which are obtained via a scaling procedure for the correlation energy of the He atom to obtain the best agreement with the accurate value. In this manner, Brual and Rothstein (1978, 1979) ensured the agreement of the correlation energy for a particular atomic system and nullified the incorrect description of the intermediate density region adopted in the GK approach (Kim and Gordon, 1974). Brual and Rothstein suggested that the parameters α and β are universal (Table VI).

In the framework of the GK approach and its various modifications, the correlation energy is described inadequately at large R, because the long-range behavior of E_{corr} is nearly independent of the electron density. To avoid this difficulty, it was proposed to add E_{disp} as the long-range

TABLE VI

CORRELATION ENERGIES FOR RARE GAS ATOMS VIA EQ. (6)[a]

Atoms	GK via Eq. (9)	McW via Eq. (10)	BR via Eq. (11)[b]	Accurate value
He	−0.1165	−0.1286	−0.042045	−0.042045
Ne	−0.7574	−0.7828	−0.3567	−0.381
Ar	−1.457	−1.431	−0.722	−0.732
Kr	−3.334	−3.083	−1.789	

[a] Brual and Rothstein (1979).

[b] $\alpha = 9.810$ and $\beta = 21.437$.

correlation energy term (Gordon and Kim, 1972; Rae, 1973, 1975; Cohen and Pack, 1974):

$$E_{\text{corr}}^{\text{GKR}}(R) = E_{\text{corr}}^{\text{st}}(R) + E_{\text{disp}}^{\text{GKR}}(R) \tag{12}$$

where for $E_{\text{disp}}^{\text{GKR}}(R)$ we have

$$E_{\text{disp}}^{\text{GKR}}(R) = -\sum_{n=3}^{n'} f_n C_{2n} R^{-2n} \tag{13}$$

with the switching function f_n defined as follows:

$$f_n = 1, \qquad n < n' \tag{14a}$$

$$f_{n'}^{-1} = 1 + \exp[-(2R - R_{n'-1,n'} + R_{n',n'+1})/2(R_{n',n'+1} - R_{n'-1,n'})],$$
$$n = n' \tag{14b}$$

and

$$R_{i,j} = (C_{2j}/C_{2i})^{1/2} \tag{14c}$$

In particular, for a given R, one can obtain that

$$R_{n'-1,n'} \le R \le R_{n',n'+1} \qquad \text{for} \quad n' > 3 \tag{14d}$$

Cohen and Pack (1974) estimate E_{corr} as follows:

$$E_{\text{corr}}^{\text{CP}}(R) = \begin{cases} [E_{\text{disp}}^{\text{CP}}(R_e)/E_{\text{corr}}^{\text{st}}(R_e)]E_{\text{corr}}^{\text{st}}(R), & R < R_e \\ E_{\text{disp}}^{\text{CP}}(R), \qquad R \ge R_e \end{cases} \tag{15}$$

with

$$E_{\text{disp}}^{\text{CP}}(R) = -\sum_{n=3}^{5} C_{2n}/R^{2n}$$

and $R = R_e$ is taken as the value of R for which $E_{\text{disp}}^{\text{CP}}(R)/E_{\text{corr}}^{\text{st}}(R)$ has a minimum.

Brual and Rothstein (1978, 1979) suggested the following form, which is close to Eqs. (13) and (14):

$$E_{\text{disp}}^{\text{BR}}(R) = -\sum_{n=3}^{n'} g_n C_{2n} R^{-2n} \tag{17}$$

where $g_n(R)$ is the linearized switching function:

$$g_n(R) = \begin{cases} 1, & n < n' \\ (R - R_{n'-1,n'})/(R_{n',n'+1} - R_{n'-1,n'}), & n = n' \end{cases} \tag{18}$$

and $R_{i,j}$ is given by Eq. (14c).

Recently, Radzio-Andzelm (1981) proposed the well-known form for $E_{\text{disp}}(R)$:

$$E_{\text{disp}}(R) = -f(R) \sum_{n=3}^{5} C_{2n}/R^{2n} \tag{19}$$

where the damping function $f(R)$ was given by Duquette *et al.* (1978). Notice that, as is well known, this expression correctly describes $E_{\text{disp}}(R)$.

Let us next discuss the exchange energy density functional. In the Gordon–Kim approach, $E^{\text{st}}_{X,\text{exch}}$ is written in the following general form, similar to $E^{\text{st}}_{X,\text{corr}}$:

$$E^{\text{st}}_{X,\text{exch}} = \int \varepsilon_{\text{exch}}[\rho_X(\mathbf{r})]\rho_X(\mathbf{r})\, d\mathbf{r} \tag{20}$$

with (Gordon and Kim, 1972; Kim and Gordon, 1974)

$$\varepsilon^{\text{GK}}_{\text{exch}}[\rho_X(\mathbf{r})] = -(3/4)(3/\pi)^{1/3}[\rho_X(\mathbf{r})]^{1/3} \tag{21}$$

which should be compared with Eq. (4). This analytical form for $\varepsilon_{\text{exch}}[\rho_X(\mathbf{r})]$ provides an incorrectly large value of the binding energy for atoms with a small number of electrons. To avoid this discrepancy, Rae (1973) corrected $\varepsilon^{\text{GK}}_{\text{exch}}$ by eliminating the self-exchange contribution to the density functional. He suggested that

$$\varepsilon^{\text{GKR}}_{\text{exch}}[N;\, \rho_X(\mathbf{r})] = \gamma(N)\,\varepsilon^{\text{GK}}_{\text{exch}}[\rho_X(\mathbf{r})] \tag{22}$$

with

$$\gamma(N) = 1 - (8/3)\,\delta + 2\,\delta^2 - (1/3)\,\delta^4 \tag{23}$$

and δ is the solution of the equation

$$(4N)^{-1} = \delta^3[1 - (9/8)\,\delta + (1/4)\,\delta^3] \tag{24}$$

where N is the total number of the electrons in the whole system AB. Rae (1975) carried out a linear extrapolation on γ such that

$$\gamma(N) = [\rho_{\text{A}}\gamma(N_{\text{A}}) + \rho_{\text{B}}\gamma(N_{\text{B}})]/\rho_{\text{AB}} \tag{25}$$

where N_{A} and N_{B} are the numbers of electrons of the atoms (or in the outer shells) A and B, respectively. However, Rae's correction to $\varepsilon_{\text{exch}}[\rho_X(\mathbf{r})]$ has some problems, as pointed out by Kolos and Radzio (1978) and by Brual and Rothstein. The latter authors proposed the modified Handler formula (Handler, 1974) for $\varepsilon_{\text{exch}}$ (Brual and Rothstein, 1978, 1979)

$$\begin{aligned}\varepsilon^{\text{BR}}_{\text{exch}}[N;\, \rho_X(\mathbf{r})] = {} & -5.74449[\rho_X(\mathbf{r})]^{2/3} \\ & \times \{1 + a[\rho_X(\mathbf{r})]^p + b[\rho_X(\mathbf{r})]^q + c[\rho_X(\mathbf{r})]^r \\ & + d[\rho_X(\mathbf{r})]^s\}^{-Q}\end{aligned} \tag{26}$$

where

$$a = 117.15510N^{-0.46802}$$
$$b = 25.55999N^{-0.37267}$$
$$c = 42.11950N^{0.18459}$$
$$d = [11.48898/(0.162748N^{1.27935})]^{1.5s}$$
$$p = 0.48100N^{0.10137}$$
$$q = 0.23273N^{-0.024536}$$
$$r = 0.44330N^{0.026373}$$
$$s = 1.072N^{0.031}$$
$$Q = 2/3s$$

and $N = (N_A + N_B)/2$. Finally we define (Brual and Rothstein, 1978, 1979)

$$E^{\mathrm{st,BR}}_{\mathrm{exch}}(R) = \int \{\rho_{AB}(\mathbf{r})\varepsilon^{\mathrm{BR}}_{\mathrm{exch}}[N;\, \rho_{AB}(\mathbf{r})] - \rho_A \varepsilon^{\mathrm{BR}}_{\mathrm{exch}}[N;\, \rho_A(\mathbf{r})] - \rho_B(\mathbf{r})\varepsilon^{\mathrm{BR}}_{\mathrm{exch}}[N;\, \rho_B(\mathbf{r})]\}\, d\mathbf{r} \tag{27}$$

Radzio-Andzelm (1981) divides $E^{\mathrm{st}}_{\mathrm{exch}}$ into two parts

$$E^{\mathrm{st}}_{X,\mathrm{exch}} = E^{\mathrm{st(1)}}_{X,\mathrm{exch}} + E^{\mathrm{st(2)}}_{X,\mathrm{exch}} \tag{28}$$

where $E^{\mathrm{st(1)}}_{X,\mathrm{exch}}$ determines the homogeneous statistical term in the GK approach, Eq. (21), and the gradient term is as follows:

$$E^{\mathrm{st(2)}}_{X,\mathrm{exch}} = -3\beta(3/\pi)^{1/3} \int [\nabla\rho_X(\mathbf{r})]^2[\rho_X(\mathbf{r})]^{-4/3} \times \exp\{-\gamma[\nabla\rho_X(\mathbf{r})]^2[\rho_X(\mathbf{r})]^{-8/3}\}\, d\mathbf{r} \tag{29}$$

where the exponential damping functional eliminates the divergent behavior of the gradient term at a large R (Herman *et al.*, 1969, 1970). In particular, for noble gas diatomic interactions $\beta = 0.0001$ and $\gamma = 0.0002$. In this connection, we note that in our opinion the application of suitably modified gradient corrections will be very useful to obtain correct results in the study of diatomic interactions.

Finally, let us comment in brief on the kinetic term $E^{\mathrm{st}}_{\mathrm{kin}}$. As is well known, the kinetic energy in the statistical theory can be improved by adding some inhomogeneity corrections; in particular, the second-order gradient correction was first introduced by Weizsäcker. However, this term is not successful (Brual and Rothstein, 1978; Radzio-Andzelm, 1981; Shih, 1979). To solve this problem, Kolos and Radzio (1978) applied the quantum-mechanical formula by Fröman and Löwdin (1960) that is obtained analytically without any difficulties.

In concluding the discussions of this section, we would like to mention the study of noble gas diatomic interactions via the MS-$X\alpha$ approach (Bellum and Micha, 1974; Konowalow *et al.*, 1972; Trickey *et al.*, 1973). The results obtained emphasize the validity of the theory and its modifications to provide the correct description of diatomic interactions in the short-range region of R. Nevertheless, this approach has not advanced recently. Therefore, the theoretical description of diatomic interaction in the framework of the density functional theory is as yet far from being complete. An effort has been made in this section to provide, above all, the correct description of diatomic interactions in the intermediate density region, where the basic equation, Eq. (8), of all theoretical approaches is not sufficiently correct. Therefore, the problem of introducing a finer separation of ρ_{AB} into ρ_A and ρ_B arises and is of great importance.

XI. Mathematical Grounds for Fitting Experimental Data: Rydberg–Klein–Rees Approach

Adequate reproduction of the form of the diatomic potential from experimental data is a very difficult problem. Some procedures for resolving this problem were examined in detail by Stwalley (1973a), Buck (1975), Carney *et al.* (1978), and Le Roy and Carley (1980) (see also references therein).

One of the most powerful methods for constructing diatomic potentials is the so-called Rydberg–Klein–Rees approach (Rydberg, 1931; Klein, 1932; Rees, 1947) (or, as adopted in the literature, the RKR method). The RKR approach provides more accurate diatomic potentials based on the use of data on determining the inner and outer turning points (see Section I) for classical motion for a given energy level and a given vibrational quantum number. The RKR procedure is systematic and accurate, and at the same time it provides information about diatomic potentials numerically at a series of points instead of analytically via the expressions discussed earlier. In our discussion of this approach, we will follow the papers by Jarmain (1960, 1971) (see also, Kirschner and Watson, 1974).

For classical turning points R_1 and R_2 of a given vibrating diatomic molecule with an energy U, we have (Klein, 1932; Jarmain, 1960)

$$R_{1,2}(U) = [(f/g) + f^2]^{1/2} \pm f \tag{1}$$

where

$$f = \partial S/\partial U|_{\kappa=0}, \qquad g = -\partial S/\partial \kappa|_{\kappa=0} \tag{2}$$

and the auxiliary function $S = S(U, \kappa)$ is defined as follows:

$$S(U, \kappa) = \pi^{-1}(2\mu)^{-1/2} \int_0^{I'} [U - E(I, \kappa)]^{1/2}\, dI \tag{3}$$

where $E(I, \kappa)$ is the sum of vibrational and rotational energies for any levels up to U, $I = h(v + \frac{1}{2})$ is an action variable, $\kappa = (8\pi^2\mu)^{-1}[h^2 J(J + 1)]$, J is the rotational quantum number, μ is the reduced mass of a given diatomic, and $I = I'$ for $E = U$.

For rotationless levels, putting $V = v + \frac{1}{2}$, we easily obtain

$$f(U) = h(2\pi)^{-1}(2\mu)^{-1/2} \int_0^{V'} [U - E(V, \kappa)]^{-1/2}\, dV \tag{4}$$

$$g(U) = h(2\pi)^{-1}(2\mu)^{-1/2} \int_0^{V'} [\partial E/\partial \kappa][U - E(V, \kappa)]^{-1/2}\, dV \tag{5}$$

Taking into account the Herzberg expression [Eq. (I.9)], Eqs. (4) and (5) are written up to the quadratic term, V^2, as follows (Jarmain, 1960):

$$f = r_e B_e^{1/2} \int_0^{V'} [U - (\omega_e V - \omega_e x_e V^2 + \cdots)]^{-1/2}\, dV \tag{6}$$

$$\begin{aligned} g = (r_e B_e^{1/2})^{-1}\Big\{&B_e \int_0^{V'} [U - (\omega_e V - \omega_e x_e V^2 + \cdots)]^{-1/2}\, dV \\ &- \alpha_e \int_0^{V'} V[U - (\omega_e V - \omega_e x_e V^2 + \cdots)]^{-1/2}\, dV \\ &+ \gamma_e \int_0^{V'} V^2[U - (\omega_e V - \omega_e x_e V^2 + \cdots)]^{-1/2}\, dV\Big\} \end{aligned} \tag{7}$$

Finally, Klein proposed a simple formula for calculating diatomic potentials except for the near dissociation limit (Jarmain, 1960)

$$R_{1,2}(V)/R_e = [S_1/(S_1 + S_2) + (f/R_e)^2]^{1/2} \pm f/R_e \tag{8}$$

where

$$S_1(V) = 1 + \sum_{n=1}^{\infty} b_n V^n \tag{9}$$

$$S_2(V) = \sum_{n=1}^{\infty} d_n V^n \tag{10}$$

and

$$f/R_e = 2(B_e/\omega_e)^{1/2} V^{1/2} S_1(V) \tag{11}$$

In particular, we have

$$\begin{aligned} R_{1,2}(V)/R_e = {} & 1 + [2(B_e/\omega_e) + (1/3)(\alpha_e/B_e)]V + [(10/3)k(B_e/\omega_e) \\ & - 2(B_e/\omega_e)^2 - (2/3)(\alpha_e/\omega_e) + (1/45)k(\alpha_e/B_e) \\ & + (1/6)(\alpha_e/B_e)^2 - (4/15)(\gamma_e/B_e)]V^2 + \cdots \\ & \pm 2(B_e/\omega_e)^{1/2}\{1 + (5/6)kV + [(43/40)k^2 \\ & - (11/10)m]V^2 + \cdots\}V^{1/2} \end{aligned} \tag{12}$$

where

$$k = \omega_e x_e/\omega_e, \qquad m = \omega_e y_e/\omega_e$$

In the framework of the RKR approach, let us consider the Dunham power-series expansion [Eq. (II.1)], invert it, and expand ξ_D as a function of $U^{1/2}$. We then have (Sandeman, 1940)

$$\xi_D = \pm[(U - U_e)/a_0^D]^{1/2}\left\{1 + \sum_{n=1}^{\infty}(\pm 1)^n c_n[(U - U_e)/a_0^D]^{n/2}\right\} \tag{13}$$

where

$$\begin{aligned} c_1 &= (1/2) + (1/12)(\omega_e/B_e)(\alpha_e/B_e) \\ c_2 &= (1/3)(\omega_e x_e/B_e) \\ c_3 &= (1/2) - 2c_1 + (3/5)c_2 + (3/2)c_1^2 + (4/5)c_1c_2 - (1/60)(\omega_e/B_e)^2(\gamma_e/B_e) \\ c_4 &= (9/5)c_2^2 - (1/10)(\omega_e/B_e)(\omega_e y_e/B_e) \\ 14c_5 &= (9 + 10c_1)c_4 - 2(14 - 21c_1 - 11c_2)c_3 \\ &\quad + (17 - 12c_1 - 6c_2 - 33c_1^2 - 18c_1c_2)c_2 \\ &\quad - 14(3 - 5c_1 + 2c_1^2)c_1 + 7 \\ 7c_6 &= 30c_2c_4 - 27c_2^3 + (1/5)(\omega_e/B_e)^3(\omega_e z_e/\omega_e) \\ 21c_7 &= 14(1 + c_1)c_6 - 7(6 - 9c_1 - 7c_2)c_5 \\ &\quad + [(55/2) - 26c_1 - 27c_2 + 29c_3 - (87/2)c_1^2 - 60c_1c_2]c_4 \\ &\quad - [63 - 210c_1 - 14c_2 - (63/2)c_3 + 126c_1^2 + 147c_1c_2 + 65c_2^2]c_3 \\ &\quad + [(77/2) - 105c_1 - (5/2)c_2 - 35c_1^2 + 24c_1c_2 + (27/2)c_2^2 + 98c_1^3 \\ &\quad + (195/2)c_2^2c_2 + 54c_1c_2^2]c_2 \\ &\quad - [84 - (441/2)c_1 + 210c_1^2 - (105/2)c_1^3]c_1 + (21/2) \\ c_8 &= 5c_2c_6 + (50/21)c_4^2 - 15c_2^2c_4 + 9c_2^4 \end{aligned} \tag{14}$$

and so on.

If we substitute U as the function of powers $(v + \frac{1}{2})$ and take into account Eqs. (14), then it follows from Eq. (13) that to a first approximation, the RKR-potential is exactly the same as the D-potential (Jarmain, 1960). The Sandeman series has an extended region of convergence relative to the D-series (Jarmain, 1960; see also, Hurley, 1962a). In 1966, Davies and Vanderslice (1966) proved the absolute convergence of series for the classical turning points up to the dissociation limit (see also, Beckel and Engelke, 1968). Le Roy estimated the error in determining the turning points from the experimental data (Le Roy, 1970). Huffaker (1977) proposed the analytical form of the RKR-potential that allows inclusion of higher order WKB corrections. This form was applied by Huffaker (1978) to demonstrate the explicit connection between the RKR approach and the perturbed Morse oscillator potential. Stwalley (1973b) carried out a detailed analysis about the serious disagreement between the diatomic potential functions obtained by the RKR approach and *ab initio* method, in particular, for the B $^1\Sigma_u^+$ state of H_2 (Kolos, 1970).

Therefore, the RKR approach provides a semiclassical method for obtaining turning points and constructing a diatomic potential. And it is perhaps worth mentioning that in general the quantum-mechanical energy levels obtained by the RKR method will not precisely reproduce the same potential (Stwalley, 1973a). In this connection it would be desired to develop an iterative procedure involving the RKR approach as a starting point—a "zeroth order" potential—of the procedure, corrected further by corresponding quantum-mechanical formulas (Stwalley, 1973a). Some approaches have been proposed to improve the RKR-potential (Kaiiser, 1970; Kirschner and Watson, 1974; Vidal and Scheingraber, 1977; Watson, 1979; Gouedard and Vigue, 1983).

XII. Concluding Remarks

In the review presented, the authors have considered the modern state of the theory of diatomic interactions in two comparative ways, one from the energetic and force-theoretical viewpoints, and the other from the mathematical and interpretative viewpoints. Undoubtedly, these points of view enhance each other. Also, these viewpoints have been studied in the framework of two complementary subspaces of the whole phase space of a given diatomic molecule, the position and the momentum subspaces. Probably it is of interest to study the theory of diatomic interactions based on the whole phase space. Of course, such an approach will be also useful in the study of the dynamical aspects of diatomic interactions.

An extensive amount of work has been devoted to developing the theory of diatomic interactions, and in fact has resulted in many great successes. In particular, among the many theoretical problems in diatomic interaction theory, which in their diversity account for the varied approaches to finding solutions, it is evident that a reasonably accurate and correct solution has been obtained for the diatomic potential function, i.e., a tremendous step has been taken toward achieving the best diatomic potential (see, in particular, Epstein, 1981a, and references therein). Through this, a large number of the empirical diatomic potential functions have been proposed. In the authors' opinion, the most important and pragmatic problem, even the cornerstone, of the theory of diatomic interactions consists in addressing the following question: *How well does a given empirical potential function represent, provide, and predict the relevant observed data?* Evidently, this problem may be divided into two self-evident and important subproblems: (1) A choice of a suitable, analytical, and not so complex form for the empirical potential function, which satisfies the usual quantum-mechanical criteria (see Section I) and which describes adequately the nature of the corresponding chemical bonding. (2) A fitting procedure for parameters of this potential function.

Let us assume that the reader knows by this time how to resolve the first subproblem. Hence, let us consider the second one. In order to establish the general validity of the proposed function, the reader must carry out the following test procedure:

1. Compare the theoretical curve with the experimental one, if the latter exists.
2. Substitute the proposed potential function into the Schrödinger equation and solve it as exactly as possible in order to find the vibrational–rotational wave functions and the corresponding eigenenergies.
3. Elucidate the spectroscopic constants that were not used in the fitting procedure of the proposed function and compare them with the real values.
4. Compare the transition intensities obtained with the experimental data.
5. Compare the thermophysical quantities such as, for example, the second virial coefficients, and estimate deviations.

And so on; the fitting procedure is therefore of great importance in the theory of diatomic interactions. However, nothing is perfect and the fitting procedures applied now by many authors still have theoretical problems, of which a detailed analysis has been recently done by Kaplan (1982). Here we would like to discuss the most general, in our opinion, fitting procedure. (The grounds for this procedure were outlined with Dr. V. A. Mazur.) The statement of the problem is as follows.

A real situation, which may be observed usually under the reconstruction of the given potential parameters on the basis of a variety of experimental data, for example, data on the second virial coefficient or on the molecular beam scattering, is characterized by the following statement: "An average deviation of quantities obtained from the experimental ones must be in a neighborhood of an order of ε." This is the typical statement of the so-called diffuse criterion, which is described by a fuzzy set. Such fuzzy set is defined by the following function:

$$f: X \rightarrow L$$

where L is a lattice.

The term "fuzzy set" was first introduced by Zadeh (1965). This is the most adequate model for a description of nondefinitive situations which do not possess sharp boundaries. The mathematical model of the conflict situation, characterized in that the parameters of the empirical interaction potential model X_A obtained on the basis of one set of properties do not correspond to the parameters X_B obtained from another set of properties, may be represented as a set X of the alternative subsets of parameters with their fuzzy subsets, which map the unsharply formulated criteria; i.e., as the system $(X, f_1, f_2, \ldots, f_R, L)$. In the framework of this problem, one needs to construct the following function in order to account for all possible criteria:

$$D = f_1 \wedge f_2 \wedge \cdots \wedge f_R$$

A search of parameters of the model X_{opt}, which provide the optimal, in a definite sense, approximation to the set of simultaneously unachieved properties, leads to the multicriteria optimization problem. It is formulated as follows: To find

$$\text{opt}\, D\{[f_1(x) \wedge f_2(X) \wedge \cdots \wedge f_R(X)] | X \in \Omega\}$$

where $f_\alpha(X)$ is some local criterion characterizing a "distance" between an observed property (α) and its model property, and Ω is a region of permissible value of X. For example, the direct form of the criterion α under a determination of parameters of the empirical diatomic interaction potential, based on the second virial coefficient experimental data, may be written as follows:

$$\begin{aligned} f_\alpha &\equiv \| B_{\text{exp}}(T), B_{\text{mod}}(U(X), T) \| \\ &= \sum_i [B_i^{\text{exp}}(T) - B_i^{\text{mod}}(T)]^2 \end{aligned}$$

where

$$B_{\text{mod}}(U(X), T) = 2\pi N \int_0^\infty \{1 - \exp[\mathrm{U(X, R)/kT}]\} R^2\, dR$$

In the case of the multicriteria problems that require a resolution of the conflict between contradictory criteria, the formal definition of the optimality is absent. In order to reveal the sense of the operator "opt," it is necessary to attract additional information of subjective nature. The constructive solution of this problem leads to the following two steps: (1) finding a Paretto region Ω_K, i.e., a region in Ω where it is impossible to improve some of the criteria without making the others worthless; (2) improvement of the solution in the compromise region Ω at the expense of attraction of the heuristic information. On the basis of this information, a convolution of the vector function D into the scalar function, i.e., the secularization procedure, is carried out. There exist some approaches (Podinovskii and Nogyn, 1982; Barlet and Marks, 1974; Sobol' and Statnikov, 1981) for the determination of the compromise region. Let us discuss briefly the analytic approach (Sobol' and Statnikov, 1981), in which the compromise line is considered as a geometric set of points of tangency of level surfaces of the criteria f_α. Then the Paretto-optimal solution is considered as the formal solution of the multicriteria problem. However, it does not provide a one-to-one answer and contracts only the region of all permissible values of X. The final solution is attained by the second step when the global scalar criterion is formulated. The complete analysis of these steps in the light of the fitting problem for diatomic interaction potential parameters has been given recently (Mazur and Pochkin, 1982). Applying this approach, the authors constructed the He–He diatomic potential, which is applicable to the description of liquid and gaseous phases.

In the authors' opinion, such approach is of great interest as a mathematically correct procedure of fitting the parameters of empirical diatomic potential functions.

The authors would like to finish the present review by quoting E. R. Davidson's words:

> Strictly speaking, a potential function for a molecule is purely a theoretical intermediate in the approximate calculation of the energy levels and not experimentally observable. There would seem to be little reason, then, to speak of an "experimental" potential function. On the other hand, it is impractical, if not impossible, to compute with spectroscopic accuracy the theoretical potential functions for all molecules of physical interest. Thus it is not surprising that numerous methods have been developed for estimating the potential function from experimental data. [Davidson, 1962]

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Gap Equations and Instabilities for Extended Systems

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I. Introduction

Electronic correlation in extended systems remains a central problem despite impressive progress in recent years. For small systems a number of very powerful methods have reached a high degree of accuracy thanks to a combination of formal algebraic and numerical techniques. These include configuration interaction,[1,5] propagator methods,[2,4,5] many-body perturbation procedures,[3-5] and coupled-cluster methods.[4] For extended systems density functional methods[6,7] dominate the scene. Certain forms of correlation are taken into account by such methods, but how and to what extent are still unclear.[8]

There is, however, a method which has not been fully exploited yet, in particular for extended systems, namely the single-determinant method without any restrictions on the spin orbitals. Thanks to very important work by Fukutome and collaborators we now have a clear picture of the various possible forms of such spin orbitals, which includes, in addition to the well-known doubly filled restricted Hartree–Fock (RHF) orbitals, alternant molecular orbitals and other forms of different orbitals for different spins, Overhauser's spin density waves, as well as others. It has been known for a long time that a sufficiently general single determinant can

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account for important correlation effects in extended systems. We now have a systematic way of exploring such effects.

Single determinants without restrictions on the spin orbitals are thus worth studying for their own sake. What is perhaps more appealing is that they provide reference functions for going beyond the single-determinant level.[9] The particular procedures for optimizing single determinants to be described in this article also provide a very natural link to a different and much more general way of treating correlation, namely the Hartree–Fock–Bogoliubov method.

The purpose of the present survey is to sum up some recent developments, which both help us to see the connections between certain concepts and to develop computational procedures. In Section II we set the stage with Fukutome's classification of possible variationally determined spin orbitals in a single determinant. In Section III we discuss the important concept of pairing, which we think of here primarily as a procedure for finding solutions to the general Hartree–Fock equations when the restricted Hartree–Fock equations are known. The pairing concept has, however, important implications also in other connections. A complete investigation of a variational problem requires a study of the character of the extrema defined by setting the first variation equal to zero. In Section IV we present a stability analysis for the single-determinant problem which takes advantage of the pairing concept. The final variation built on pairing leads to a so-called gap equation which is derived and discussed in Section V. In Section VI we describe certain applications of these procedures and in the last section we discuss their connections to methods of the coupled-cluster and Hartree–Fock–Bogoliubov type.

We want to stress that the present article is not intended to present the history of or to give a detailed account of concepts such as pairing and gap equations. Our aim is only to stress that such concepts, which have already been so useful in nuclear physics and certain parts of solid-state physics, should be further exploited for the study of electronic correlation in extended systems.

II. The Fukutome Classes

We begin with a study of certain symmetry properties of Slater determinants built up of general spin orbitals

$$\psi_k(x) = \phi_{k1}(\vec{r})\alpha(\zeta) + \phi_{k2}(\vec{r})\beta(\zeta), \tag{2.1}$$

with orbital components ϕ_{k1} and ϕ_{k2}, which are in general complex. Throughout this article the symbol x will be used for the combined coordinate $(\vec{r}, \zeta)$ with four components. It is practical to write Eq. (2.1) in *spinor* *form:*

$$\psi_k = (\alpha\beta)\begin{bmatrix}\phi_{k1}\\ \phi_{k2}\end{bmatrix} = (\alpha\beta)\boldsymbol{\Phi}_k. \tag{2.2}$$

A Slater determinant for an N-electron system is a function of the form

$$D = \frac{1}{\sqrt{N!}}\det\{\psi_1(x_1),\ \psi_2(x_2),\ \ldots,\ \psi_N(x_N)\}, \tag{2.3}$$

where we can assume the spin orbitals to be orthonormal

$$\int \psi_k^*(x)\psi_l(x)\,dx = \delta_{kl}. \tag{2.4}$$

The determinant is best characterized by the associated Fock–Dirac density matrix.[10]

$$\rho(x, x') = \sum_{k=1}^{N} \psi_k(x)\psi_k^*(x'), \tag{2.5}$$

with the properties

$$\boldsymbol{\rho}^2 = \boldsymbol{\rho}, \tag{2.6}$$

or in "long hand"

$$\int \rho(x, x'')\rho(x'', x')\,dx'' = \rho(x, x'), \tag{2.7}$$

and

$$\mathrm{Tr}\,\boldsymbol{\rho} = \int \rho(x, x)\,dx = N. \tag{2.8}$$

Using the spinor form (2.2) we can go from the spin orbital form (2.5) of the Fock–Dirac matrix to the orbital form:

$$\rho = (\alpha\beta)\sum_{k=1}^{N}\boldsymbol{\Phi}_k\boldsymbol{\Phi}_k^\dagger\begin{bmatrix}\alpha\\ \beta\end{bmatrix} = (\alpha\beta)\mathbf{Q}\begin{bmatrix}\alpha\\ \beta\end{bmatrix}. \tag{2.9}$$

$\mathbf{Q}$ is thus a 2×2 matrix with elements depending on the two spatial variables $\vec{r}$ and $\vec{r}\,'$:

$$\mathbf{Q}(\vec{r}, \vec{r}\,') = \sum_{k=1}^{N}\boldsymbol{\Phi}_k(\vec{r})\boldsymbol{\Phi}_k^\dagger(\vec{r}\,') = \begin{bmatrix}\rho_{11}(\vec{r}, \vec{r}\,') & \rho_{12}(\vec{r}, \vec{r}\,')\\ \rho_{21}(\vec{r}, \vec{r}\,') & \rho_{22}(\vec{r}, \vec{r}\,')\end{bmatrix}, \tag{2.10}$$

with

$$\rho_{ij}(\vec{r}, \vec{r}\,') = \sum_{k=1}^{N}\phi_{ki}(\vec{r})\phi_{kj}^*(\vec{r}\,'). \tag{2.11}$$

In the special RHF case when the spin orbitals are simple products of orbitals and spin functions, and all the orbitals are doubly filled, we have

$$\rho_{11} = \rho_{22}; \qquad \rho_{12} = \rho_{21} = 0. \tag{2.12}$$

The orbital form of the idempotency relation (2.6) is obtained by integrating over the spin variables:

$$\int \mathbf{Q}(\vec{r}, \vec{r}\,'')\mathbf{Q}(\vec{r}\,'', \vec{r}\,')\, dv'' = \mathbf{Q}(\vec{r}, \vec{r}\,'), \tag{2.13}$$

or

$$\sum_{k=1}^{2} \int \rho_{ik}(\vec{r}, \vec{r}\,'')\rho_{kj}(\vec{r}\,'', \vec{r}\,')\, dv'' = \rho_{ij}(\vec{r}, \vec{r}\,'); \qquad i, j = 1, 2. \tag{2.14}$$

Similarly we get the orbital form of (2.8)

$$\operatorname{Tr} \boldsymbol{\rho} = \operatorname{Tr} \mathbf{Q} = \int [\rho_{11}(\vec{r}, \vec{r}) + \rho_{22}(\vec{r}, \vec{r})]\, dv = N. \tag{2.15}$$

From the point of view of interpretation it is preferable to write the orbital form of the Fock–Dirac matrix in terms of the *number density matrix*

$$N(\vec{r}, \vec{r}\,') = \int \rho(\vec{r}, \zeta; \vec{r}\,', \zeta)\, d\zeta, \tag{2.16}$$

and the *spin density matrix vector*

$$\vec{S}(\vec{r}, \vec{r}\,') = \int \vec{s}\rho(x, x')\, d\zeta. \tag{2.17}$$

Here

$$\vec{s} = \vec{e}_x s_x + \vec{e}_y s_y + \vec{e}_z s_z, \tag{2.18}$$

is the spin operator for one electron. In (2.17) we use the ordinary convention that the operator $\vec{s}$ works on the unprimed coordinate ζ, after which we set $\zeta' = \zeta$ and integrate.

From the properties of the spin functions we get, writing $S_1 = S_x$, $S_2 = S_y$, $S_3 = S_z$,

$$\begin{aligned} N(\vec{r}, \vec{r}\,') &= \rho_{11}(\vec{r}, \vec{r}\,') + \rho_{22}(\vec{r}, \vec{r}\,'); \\ S_1(\vec{r}, \vec{r}\,') &= \tfrac{1}{2}[\rho_{12}(\vec{r}, \vec{r}\,') + \rho_{21}(\vec{r}, \vec{r}\,')]; \\ S_2(\vec{r}, \vec{r}\,') &= \tfrac{i}{2}[\rho_{12}(\vec{r}, \vec{r}\,') - \rho_{21}(\vec{r}, \vec{r}\,')]; \\ S_3(\vec{r}, \vec{r}\,') &= \tfrac{1}{2}[\rho_{11}(\vec{r}, \vec{r}\,') - \rho_{22}(\vec{r}, \vec{r}\,')]. \end{aligned} \tag{2.19}$$

Inverting (2.19) we can then express $\mathbf{Q}$ as

$$\mathbf{Q} = \begin{bmatrix} \tfrac{1}{2}N + S_3 & S_1 - iS_2 \\ S_1 + iS_2 & \tfrac{1}{2}N - S_3 \end{bmatrix} = \tfrac{1}{2}N \cdot \mathbf{1} + \vec{\sigma} \cdot \vec{S}. \tag{2.20}$$

Here $\vec{\sigma}$ is the vector with the Pauli matrices

$$\sigma_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; \qquad \sigma_2 = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}; \qquad \sigma_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \tag{2.21}$$

as components.

Given a Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \sum_{i=1}^{N} h_i + \tfrac{1}{2} \sum_{i,j}{}' g_{ij}, \tag{2.22}$$

we can optimize the determinant (2.3) by means of the variation principle

$$\delta \left\{ \frac{\langle D|\mathcal{H}|D\rangle}{\langle D|D\rangle} \right\} = 0, \tag{2.23}$$

which leads to the Hartree–Fock equations

$$\mathcal{H}_{\text{eff}}(1)\psi_k(x_1) = \varepsilon_k \psi_k(x_1); \tag{2.24}$$

$$\mathcal{H}_{\text{eff}}(1) = h_1 + \int dx_2 g_{12}(1 - P_{12})\rho(x_2, x_2'), \tag{2.25}$$

for the spin orbitals.[10] For these effective one-electron equations with the general spin orbitals (2.1) we propose the term *general Hartree–Fock equations* (*GHF*).

It is customary to speak about unrestricted Hartree–Fock equations (UHF) when one or more of the restrictions associated with RHF are released. In order to avoid misunderstandings we prefer to use the term GHF for the most general case, which contains both RHF and the various types of UHF as special cases.

Multiplying (2.24) from the left by

$$\begin{bmatrix} \alpha(\zeta_1) \\ \beta(\zeta_1) \end{bmatrix} \tag{2.26}$$

and integrating over ζ_1, we get the *general orbital form* of the GHF equations:

$$[F(1) \cdot \mathbf{1} + \vec{\sigma} \cdot \vec{G}(1)]\Phi_k(\vec{r}_1) = \varepsilon_k \Phi_k(\vec{r}_1), \tag{2.27}$$

with

$$\begin{aligned} F(1) &= h_1 + \int dv_2\, g_{12} N(\vec{r}_2, \vec{r}_2) - \frac{1}{2} \int dv_2\, g_{12} P^r_{12} N(\vec{r}_2, \vec{r}_2'); \\ \vec{G}(1) &= -\int dv_2\, g_{12} P^r_{12} \vec{S}(\vec{r}_2, \vec{r}_2'). \end{aligned} \tag{2.28}$$

Similarly we have the spin orbital form of the total GHF energy

$$E_{\mathrm{GHF}} = \mathcal{H}_0 + \int \mathscr{h}_1 \rho(x_1, x_1') \, dx_1 + \frac{1}{2} \int dx_1 \, dx_2 \, \mathscr{g}_{12}(1 - P_{12}) \rho(x_1, x_1') \rho(x_2, x_2') \tag{2.29}$$

and the associated orbital form (provided $\mathscr{h}_1$ and $\mathscr{g}_{12}$ are spin independent)

$$E_{\mathrm{GHF}} = \mathcal{H}_0 + \int \mathscr{h}_1 N(\vec{r}_1, \vec{r}_1') \, dv_1 + \frac{1}{2} \int dv_1 \, dv_2 \, \mathscr{g}_{12} N(\vec{r}_1, \vec{r}_1) N(\vec{r}_2, \vec{r}_2) - \int dv_1 \, dv_2 \, \mathscr{g}_{12} \left[\frac{1}{4} N(\vec{r}_1, \vec{r}_2) N(\vec{r}_2, \vec{r}_1) + \vec{S}(\vec{r}_1, \vec{r}_2) \cdot \vec{S}(\vec{r}_2, \vec{r}_1) \right]. \tag{2.30}$$

Fukutome[11] in a series of papers has made a thorough analysis of the symmetry properties of the GHF spin orbitals. As pointed out by Löwdin,[12] there is no reason why a solution D of (2.23) should be symmetry adapted to the symmetry of the Hamiltonian. We can impose symmetry constraints on the spin orbitals, but that will in general raise the total energy. To characterize this situation Löwdin has coined the term "symmetry dilemma."

Even though the spin orbitals obtained from (2.23) in general do not have the full symmetry of the Hamiltonian, they may have *some* symmetry properties. In order to study these Fukutome considered the transformation properties of solutions of (2.24) with respect to spin rotations and time reversal. Whatever spatial symmetry the system under consideration has, its Hamiltonian always commutes with these operators. As we will see, the effective one-electron Hamiltonian (2.25) in general only commutes with some of them, since it depends on these solutions themselves via the Fock–Dirac matrix.

A spin rotation around an axis characterized by the unit vector $\vec{e}$ by the angle ϑ transforms the spinor $\mathbf{\Phi}$ to

$$\mathbf{\Phi}^u = \mathbf{u}(\vec{e}, \vartheta)\mathbf{\Phi} = \left[\mathbf{1} \cdot \cos \frac{\vartheta}{2} + i(\vec{\sigma} \cdot \vec{e}) \sin \frac{\vartheta}{2} \right] \mathbf{\Phi}. \tag{2.31}$$

It is a unitary

$$\mathbf{u}^\dagger \mathbf{u} = \mathbf{u}\mathbf{u}^\dagger = \mathbf{1}, \tag{2.32}$$

and unimodular

$$\det \mathbf{u} = 1, \tag{2.33}$$

operation. The set of all spin rotations form a group S.

For the time-reversal operation Θ we use the definition

$$\Theta = -i\sigma_2 K, \tag{2.34}$$

where K denotes complex conjugation. Consequently a time-reversed spinor has the form

$$\boldsymbol{\Phi}^t = \Theta\boldsymbol{\Phi} = \begin{bmatrix} -\phi_2^* \\ \phi_1^* \end{bmatrix}. \tag{2.35}$$

The antiunitary operator Θ belongs to the group $T = \{\mathbf{1}, \Theta, -\mathbf{1}, -\Theta\}$, which requires the concept of corepresentations.[13,14]

The symmetry properties of the effective Hamiltonian (2.25) or (2.27) are determined by those of the Fock–Dirac matrix. If all the occupied spin orbitals are spin rotated, the orbital part of the Fock–Dirac matrix is transformed as follows:

$$\mathbf{Q}^u = \sum_{k=1}^{N} \boldsymbol{\Phi}_k^u \boldsymbol{\Phi}_k^{u\dagger} = \mathbf{u}\mathbf{Q}\mathbf{u}^\dagger = \frac{1}{2} N \cdot \mathbf{1} + \vec{\sigma} \cdot (\vec{S}\mathbf{R}). \tag{2.36}$$

Here $\mathbf{R}$ is an orthogonal 3×3 matrix defined by

$$\mathbf{u}\sigma_i\mathbf{u}^\dagger = \sum_{j=1}^{3} R_{ij}\sigma_j, \tag{2.37}$$

which connects the two-dimensional spin rotation $\mathbf{u}$ with the rotation of the three-dimensional spin density matrix vector $\vec{S}$. From (2.36) we read off

$$N^u = N; \qquad \vec{S}^u = \vec{S}\mathbf{R}. \tag{2.38}$$

Time reversal effects the Fock–Dirac matrix as follows:

$$\mathbf{Q}^t = \sum_{k=1}^{N} \boldsymbol{\Phi}_k^t \boldsymbol{\Phi}_k^{t\dagger} = \frac{1}{2} N^* \cdot \mathbf{1} + \vec{\sigma} \cdot (-\vec{S}^*), \tag{2.39}$$

which implies

$$N^t = N^*; \qquad \vec{S}^t = -\vec{S}^*. \tag{2.40}$$

Thus in general the elements of the group $G = S \times T$ do not commute with the effective one-electron Hamiltonian (2.25). Some of these operations may, however, commute with $\mathcal{H}_{\text{eff}}$ and in such a case they form a subgroup of G. That subgroup characterizes the GHF solution under study in the sense that the corresponding Fock–Dirac matrix is invariant under the elements g of the *invariance group of the GHF solution,*

$$\mathbf{Q}^g = \mathbf{Q}. \tag{2.41}$$

Consequently the spinors $\boldsymbol{\Phi}_k$ that make up $\mathbf{Q}$ must transform according to the irreducible representations or corepresentations (if the invariance group contains antiunitary operators) of the invariance group.

TABLE I

SUBGROUPS OF THE GROUP $G = S \times T$

1. $S \times T = \{S, S\Theta\}$
2. $S = \{u(\vec{e}\ \vartheta);$ all $\vec{e}$, all $\vartheta\}$
3. $T = \{1, -1, \Theta, -\Theta\}$
4. $A(\vec{e}) = \{u(\vec{e}, \vartheta);$ fixed $\vec{e}$, all $\vartheta\}$
5. $M(\vec{e}) = \{1, u(\vec{e}, \pi)\Theta;$ fixed $\vec{e}\}$
6. $A(\vec{e}) \times \Theta = \{u(\vec{e}, \vartheta), u(\vec{e}, \vartheta)\Theta;$ fixed $\vec{e}$, all $\vartheta\}$
7. $A(\vec{e})M(\vec{e}') = \{u(\vec{e}, \vartheta), u(\vec{e}, \vartheta)u(\vec{e}', \pi)\Theta;$ fixed $\vec{e}, \vec{e}'; \vec{e}\cdot\vec{e}' = 0;$ all $\vartheta\}$
8. $E' = \{1, -1\}$
   $E = \{1\}$

Following Fukutome we can therefore use the subgroup structure of G to classify the different types of GHF solutions that are possible, with respect to the properties of the number density matrix $N(\vec{r}, \vec{r}')$ and the spin density matrix vector $\vec{S}(\vec{r}, \vec{r}')$. With the trivial subgroups there are eight subgroups of G, which are denoted as indicated in Table I. Each such subgroup corresponds to a class of GHF solutions, with properties summed up in Table II.

The names and the properties of the Fukutome classes deserve some comments. Some of them are characterized by the expression "current

TABLE II

TABLE OF CLASSES FOR THE GHF SOLUTIONS[a]

	TR					
SR	*T*-Invariant		*M*-Invariant		*T–M*-Noninvariant	
S-Invariant	TICS (1)	$N^* = N$ $S = 0$			CCW (2)	$N^* \neq N$ $S = 0$
S-Axial	ASCW (6)	$N^* = N$ $\vec{S} = \vec{e}S$ $S^* = -S$	ASDW (7)	$N^* = N$ $\vec{S} = \vec{e}S$ $S^* = S$	ASW (4)	$N^* \neq N$ $\vec{S} = \vec{e}S$ $S^* \neq \pm S$
S-Torsional	TSCW (3)	$N^* = N$ $\vec{S}^* = -\vec{S}$	TSDW (5)	$N^* = N$ $S_\parallel^* = -S_\parallel$ $S_\perp^* = S_\perp$	TSW (8)	$N^* \neq N$ $\vec{S}^* \neq \pm S$

[a] Given by Fukutome.[11] $S_\parallel$ and $S_\perp$ are the projections parallel and perpendicular to S. Abbreviations: TICS, time-reversal-invariant closed shell; CCW, charge-current wave; ASCW, axial spin-current wave; ASDW, axial spin density wave; ASW, axial spin wave; TSCW, torsional spin-current wave; TSDW, torsional spin density wave; TSW, torsional spin wave. The numbers in parentheses refer to the numbering of the subgroups in Table I.

waves." This term is derived from the usual definition of the current density associated with a wave function ψ as

$$\vec{j} = \frac{ie\hbar}{2m} [\psi^* \nabla \psi - (\nabla \psi)^* \psi]. \tag{2.42}$$

Using the convention about primed and unprimed variables referred to above we can write this as

$$\vec{j}(\vec{r}) = -\frac{e\hbar}{m} \operatorname{Im}\{\nabla \psi(\vec{r}) \psi^*(\vec{r}\,')\}. \tag{2.43}$$

Given a function $\sigma(\vec{r}, \vec{r}\,')$ of density matrix type we can therefore define its current density matrix as

$$\vec{j}_\sigma(\vec{r}, \vec{r}\,') = \operatorname{Im}\{\nabla \sigma(\vec{r}, \vec{r}\,')\} \tag{2.44}$$

Separating σ into its real and imaginary parts,

$$\sigma = \sigma_1 + i\sigma_2, \tag{2.45}$$

we thus get

$$\vec{j}_\sigma(\vec{r}, \vec{r}\,') = \nabla \sigma_2(\vec{r}, \vec{r}\,'). \tag{2.46}$$

The components (2.11) of the orbital part of the Fock–Dirac matrix have the property

$$\rho_{ij}(\vec{r}, \vec{r}\,')^* = \rho_{ji}(\vec{r}\,', \vec{r}), \tag{2.47}$$

which implies

$$\rho_{ij}(\vec{r}, \vec{r})^* = \rho_{ji}(\vec{r}, \vec{r}); \qquad \rho_{ii}(\vec{r}, \vec{r}) = \rho_{ii}^*(\vec{r}, \vec{r}). \tag{2.48}$$

This means that the *number density* $N(\vec{r}, \vec{r})$ and the *spin density* $\vec{S}(\vec{r}, \vec{r})$ are real, as they should be. The nondiagonal elements of the density matrices $N(\vec{r}, \vec{r}\,')$ and $\vec{S}(\vec{r}, \vec{r}\,')$ are, however, in general complex. The description of N and $\vec{S}$ in Table II refers to the nondiagonal elements.

If $N(\vec{r}, \vec{r}\,')$ or $\vec{S}(\vec{r}, \vec{r}\,')$ has a nonvanishing imaginary part there is a corresponding current density. The charge-current wave (CCW) class, for example, has a complex number density matrix, whereas the axial spin-current wave (ASCW) class has a purely imaginary spin density matrix.

The three rows in Table II refer to properties of the spin density. In the first one it vanishes, which implies that we must have doubly filled orbitals in the corresponding determinants. The two classes TICS and CCW differ by having real and complex orbitals, respectively. In the second row of Table II there are three classes with a nonvanishing spin density *with a fixed direction*—hence the term "axial." Of these the class ASDW is most well known—one example being furnished by the alternant molecular orbitals (AMO).[15] In the third row there are three classes with a spin density, the direction of which varies in space. Overhauser's spin density waves[16] provide an example of a set of functions belonging to the class TSDW.

In Table III we sum up the implications of Table II for the spin orbitals in the different classes.[13,17]

TABLE III

SPINOR FORMS OF THE SPIN ORBITALS IN THE EIGHT FUKUTOME CLASSES

$$|\Psi\rangle = [\psi_1, \psi_2, \ldots, \psi_N] = (\alpha\beta)|\Phi\rangle$$

$$|\Phi\rangle = [\Phi_1, \Phi_2, \ldots, \Phi_N] = \begin{bmatrix} \phi_{11}, \phi_{21}, \ldots, \phi_{k1}, \ldots, \phi_{N1} \\ \phi_{12}, \phi_{22}, \ldots, \phi_{k2}, \ldots, \phi_{N2} \end{bmatrix}$$

1. T(ime) (reversal) I(nvariant) C(losed) S(hells)

$$|\Phi\rangle = \begin{bmatrix} u_1, 0, & u_2, 0, & \ldots, u_{N/2}, 0 \\ 0, & u_1, 0, & u_2, \ldots, 0, & u_{N/2} \end{bmatrix}; \qquad u_i \text{ real}$$

2. C(harge) C(urrent) W(aves)
   Same as for TICS but with complex orbitals $u_i(\vec{r})$

3. A(xial) S(pin) C(urrent) W(aves)

$$|\Phi\rangle = \begin{bmatrix} u_1, 0, & u_2, 0, & \ldots, u_{N/2}, 0 \\ 0, & u_1^*, 0, & u_2^*, \ldots, 0, & u_{N/2}^* \end{bmatrix}$$

4. A(xial) S(pin) D(ensity) W(aves)

$$|\Phi\rangle = \begin{bmatrix} u_1, 0, & u_2, 0, & \ldots, u_{N/2}, 0 \\ 0, & v_1, 0, & v_2, \ldots, 0, & v_{N/2} \end{bmatrix}; \qquad u_i, v_i \text{ real}$$

5. A(xial) S(pin) W(aves)
   Same as (4) but with complex orbitals u_i and v_i

6. T(orsional) S(pin) C(urrent) W(aves)

$$|\Phi\rangle = \begin{bmatrix} u_1, & w_1, u_2, & w_2, \ldots, u_{N/2}, & w_{N/2} \\ -w_1^*, u_1^*, & -w_2^*, u_2^*, & \ldots, -w_{N/2}^*, u_{N/2}^* \end{bmatrix}$$

7. T(orsional) S(pin) D(ensity) W(aves)

$$|\Phi\rangle = \begin{bmatrix} u_1, w_1, u_2, w_2, \ldots, u_{N/2}, w_{N/2} \\ t_1, v_1, t_2, v_2, \ldots, t_{N/2}, v_{N/2} \end{bmatrix}; \qquad u_1, w_i, t_i, v_i \text{ real}$$

8. T(orsional) S(pin) W(aves)
   Same as (7) but with complex orbitals

The symmetry analysis described in this section applies to all systems. If a system also has some kind of spatial symmetry a similar analysis can be carried out based on the direct product of the group $G = S \times T$ and the spatial symmetry group. For more information we refer to the papers by Ozaki and Fukutome.[18]

Before closing this section we also note the somewhat related studies of correlation functions and second-order density matrices by Fukutome and Hashimoto[19].

III. The Concept of Pairing

In the AMO method[15] one constructs two sets of orbitals

$$\begin{aligned} a_k(\vec{r}) &= \psi_k(\vec{r}) \cos \Theta_k + \bar{\psi}_k(\vec{r}) \sin \Theta_k; \\ \bar{a}_k(\vec{r}) &= \psi_k(\vec{r}) \cos \Theta_k - \bar{\psi}_k(\vec{r}) \sin \Theta_k, \end{aligned} \tag{3.1}$$

in order to get *different orbitals for different spins*. Here ψ_k is an RHF orbital and $\bar{\psi}_k$ is a function in the orthogonal complement of all the occupied RHF orbitals. In the unprojected AMO method used for extended systems one builds up a determinant,

$$D_{\text{AMO}} = \frac{1}{\sqrt{N!}} \det\{.\ .\ .\ a_k\alpha, \bar{a}_k\beta, .\ .\ .\}, \tag{3.2}$$

which is optimized by means of the variation principle. Usually the partners are fixed and one then determines the mixing parameters Θ_k variationally.

The AMO determinant (3.2) can be expanded in determinants containing the ψ_k and the $\bar{\psi}_k$. It is therefore equivalent to an RHF determinant with a special kind of configuration interaction, in which certain relationships between the coefficients are imposed. From that point of view D_{AMO} can describe certain correlation effects. This is particularly important for extended systems, for which the powerful CI methods developed for atoms and small molecules cannot be used.

From the GHF point of view the AMO construction (3.2) represents a particular way of approximating the solutions. Since RHF is often a good approximation, it seems natural to augment each RHF orbital with an orbital, which is orthogonal to all the occupied RHF orbitals. A large number of AMO calculations[15] show that this is indeed a reasonable procedure. More explicitly, a detailed study for the linear chain of hydrogen atoms[20] showed the AMO solutions to be indistinguishable from UHF solutions obtained directly.

The AMO construction is an example of the *concept of pairing*. Particularly for large systems this represents a very promising procedure for obtaining solutions of the GHF equations. Thanks to Fukutome's symmetry analysis we can impose certain conditions on the possible partners, once we have decided which Fukutome class we need.[13,17] Thus the GHF spin orbitals $\phi_\mu(x)$ are written

$$\phi_\mu(x) = \psi_\mu(x)u_\mu + \bar{\psi}_\mu(x)v_\mu; \qquad \mu = 1, 2, \ldots, N. \tag{3.3}$$

The mixing parameters satisfy the conditions

$$u_\mu^2 + v_\mu^2 = 1. \tag{3.4}$$

In general they are complex, but they can be chosen real,[21] provided that one includes a choice of phases in the choice of partners $\bar{\psi}_\mu$. The AMOs (3.1) provide an illustration of this point. The final spin orbitals are $a_k\alpha$ for $\mu = 2k$ and $\bar{a}_k\beta$ for $\mu = 2k + 1$. The corresponding mixing parameters are related by

$$u_{2k} = u_{2k+1}; \qquad v_{2k} = -v_{2k+1}. \tag{3.5}$$

That can also be described, however, by saying that we keep the same mixing parameters for ϕ_{2k} and ϕ_{2k+1}, but choose the partner $\bar{\psi}_k\alpha$ for ϕ_{2k} and $-\bar{\psi}_k\beta$ for ϕ_{2k+1}.

As will be discussed in Section V, the optimization of the mixing parameters can be carried out by means of the so-called gap equation. The choice of partners $\bar{\psi}_k$ is, however, open except for the condition

$$\langle\bar{\psi}_k|\psi_l\rangle = 0; \qquad k, l = 1, 2, \ldots, N. \tag{3.6}$$

If we are seeking a GHF solution in a particular Fukutome class, symmetry will impose certain conditions on $\bar{\psi}_k$.[13] One finds, for example, that functions of the class ASDW must in fact have the form (3.1). In the ASCW class the pairing must be of the form

$$\begin{aligned} \phi_{2k} &= (\psi_k u_k + \bar{\psi}_k v_k)\alpha; \\ \phi_{2k+1} &= (\psi_k u_k + \bar{\psi}_k^* v_k)\beta, \end{aligned} \tag{3.6}$$

whereas torsional spin density waves have the form

$$\begin{aligned} \phi_{2k} &= \psi_k\alpha u_k + \bar{\psi}_k\beta v_k; \\ \phi_{2k+1} &= \bar{\psi}_k^*\alpha v_k + \bar{\psi}_k^*\beta u_k. \end{aligned} \tag{3.7}$$

IV. Instabilities

The variation principle (2.23) determines an extremum, but is unable to give any information as to the character of the extremum, whether it is a maximum, a saddle point, or a local or a global minimum. Given a solution of a variational problem belonging to a particular class of trial functions, we call it *stable* if it is not possible, by variations within that class of functions, to lower the expectation value of the Hamiltonian. It is obviously very difficult to prove that a function is stable. To give examples of *instabilities,* on the other hand, is relatively easy.

The existence of an instability means that it is possible to find solutions of symmetry lower than the original one. One speaks of broken symmetry solutions. In Fukutome's classification system (Table II), the "new" solutions can belong to the same or to a different class. In the former case it is the spatial symmetry which has been lowered. If the "new" solution belongs to a different Fukutome class, the symmetry with respect to spin and/or time reversal has been lowered.

The study of instabilities of the Hartree–Fock equations is usually traced back to Thouless' book.[22] Adams[23] reformulated Thouless' stability condition in terms of density matrices. More recently Paldus and Cizek[24] and Fukutome[11] have made very important contributions to this field.

Here we will present a slightly different derivation of the conditions for instabilities,[25] which emphasizes the pairing concept as described in the previous section. Although this procedure is applicable also to more general types of wave functions we restrict the treatment here to single determinants.

We study the variation of the expectation value

$$E = \langle D|\mathcal{H}|D\rangle / \langle D|D\rangle, \tag{4.1}$$

of the total Hamiltonian with respect to a single determinant (2.3). We vary this determinant by replacing each spin orbital $\underline{\psi}_\mu(x)$ by $\phi_\mu(x)$, (3.3), which is the result of pairing $\psi_\mu(x)$ with a function $\bar{\psi}_\mu(x)$ from the orthogonal complement of all the occupied $\psi_\mu(x)$. In order to conform to the notation in Ref. 25, we will actually use

$$\psi'_\mu(x) = u_\mu^{-1}\phi_\mu(x) = \psi_\mu(x) + \bar{\psi}_\mu(x)v_\mu u_\mu^{-1} = \psi_\mu(x) + \bar{\psi}_\mu(x)c_\mu, \tag{4.2}$$

rather than ϕ_μ, and we will consider complex coefficients c_μ. We notice that $\psi'_\mu(x)$ is not normalized, which is of importance when we form the Fock–Dirac density matrix [cf. (2.5)]

$$\rho'(x, x') = \sum_{\mu=1}^{N} \phi_\mu(x)\phi_\mu^*(x') = \rho(x, x')$$

$$+ \sum_{\mu=1}^{N} [\sigma_\mu(x,x')u_\mu v_\mu + \tau_\mu(x, x')v_\mu^2]. \tag{4.3}$$

Here

$$\begin{aligned} \sigma_\mu(x, x') &= \psi_\mu(x)\bar{\psi}^*_\mu(x') + \bar{\psi}_\mu(x)\psi^*_\mu(x'); \\ \tau_\mu(x, x') &= \bar{\psi}_\mu(x)\bar{\psi}^*_\mu(x') - \psi_\mu(x)\psi^*_\mu(x'). \end{aligned} \tag{4.4}$$

Since

$$\begin{aligned} u^2_\mu &= 1/(1 + |c_\mu|^2); \\ v^2_\mu &= |c_\mu|^2/(1 + |c_\mu|^2), \end{aligned} \tag{4.5}$$

we can also write (4.3) as

$$\rho'(x, x') = \rho(x, x') + \sum_{\mu=1}^{N} \frac{1}{1 + |c_\mu|^2} [\sigma_\mu(x, x')c_\mu + \tau_\mu(x, x')|c_\mu|^2]. \tag{4.6}$$

Using the coefficients c_μ as order parameters we then get

$$\rho'(x, x') = \rho(x, x') + \delta\rho(x, x') + \delta^2\rho(x, x') + \delta^3\rho(x, x') + \cdots, \tag{4.7}$$

$$\begin{aligned} \delta\rho(x, x') &= \sum_{\mu=1}^{N} \sigma_\mu(x, x')c_\mu; \\ \delta^2\rho(x, x') &= \sum_{\mu=1}^{N} \tau_\mu(x, x')|c_\mu|^2; \\ \delta^3\rho(x, x') &= \sum_{\mu=1}^{N} \sigma_\mu(x, x')c^3_\mu; \end{aligned} \tag{4.8}$$

In terms of these quantities the varied expectation value is

$$\frac{\langle D'|\mathcal{H}|D'\rangle}{\langle D'|D'\rangle} = E + \delta E + \delta^2 E + \delta^3 E + \cdots, \tag{4.9}$$

where E is the energy (4.1) of the reference determinant and

$$\delta E = \int \mathcal{H}_{\text{eff}}(1)\delta\rho(x_1, x_1')\, dx_1; \tag{4.10}$$

$$\begin{aligned} \delta^2 E = &\int \mathcal{H}_{\text{eff}}(1)\delta^2\rho(x_1, x_1')\, dx_1 \\ &+ \frac{1}{2}\int dx_1\, dx_2\, g_{12}(1 - P_{12})\delta\rho(x_1, x_1')\delta\rho(x_2, x_2'). \end{aligned} \tag{4.11}$$

The effective one-electron operator $\mathcal{H}_{\text{eff}}(1)$ is given by (2.25).

If ρ corresponds to an extremum we have

$$\delta E = 0, \tag{4.12}$$

which gives the Hartree–Fock equations (2.24). The *character* of the extremum depends on the sign of $\delta^2 E$. If this quantity is positive for all variations we have a minimum. A not uncommon situation is that $\delta^2 E$ is positive for some and negative for some variations. We then have a saddle point, and the variations giving a negative $\delta^2 E$ give an indication where in function space one can expect to find the minimum.

The second variation $\delta^2 E$ can be written in different ways. First of all we go over to the orbital form, using (2.2, 2.9, 2.10, 2.16, 2.17) and (2.28),

$$\begin{aligned}\delta^2 E = {} & \int [F(1)\delta^2 N(\vec{r}_1, \vec{r}_1') + 2\vec{G}(1)\cdot\delta^2\vec{S}(\vec{r}_1, \vec{r}_1')]\, dv_1 \\ & + \frac{1}{2}\int dv_1\, dv_2\; g_{12}\delta N(\vec{r}_1, \vec{r}_1)\delta N(\vec{r}_2, \vec{r}_2) \\ & - \frac{1}{4}\int dv_1\, dv_2\; g_{12}\delta N(\vec{r}_1, \vec{r}_2)\delta N(\vec{r}_2, \vec{r}_1) \\ & - \int dv_1\, dv_2\; g_{12}\delta\vec{S}(\vec{r}_1, \vec{r}_2)\cdot\delta\vec{S}(\vec{r}_2, \vec{r}_1).\end{aligned} \tag{4.13}$$

In order to study $\delta^2 E$ systematically it is practical to write it as an expectation value of a matrix. We first introduce two matrices **A** and **B** with elements

$$\begin{aligned} A_{\mu\nu} &= \langle D_\mu|\mathcal{H} - E\cdot\mathbf{1}|D_\nu\rangle; \\ B_{\mu\nu} &= \langle D_{\mu\nu}|\mathcal{H} - E\cdot\mathbf{1}|D\rangle; \qquad \mu < \nu. \end{aligned} \tag{4.14}$$

Here D_ν is the determinant obtained from D when the spin orbital ψ_ν is replaced by $\bar{\psi}_\nu$, and $D_{\mu\nu}$ contains instead of ψ_μ and ψ_ν the two spin orbitals $\bar{\psi}_\mu$ and $\bar{\psi}_\nu$. Using Slater's rules we can express these quantities in terms of the spin orbitals:

$$\begin{aligned} A_{\mu\nu} &= (\bar{\varepsilon}_\mu - \varepsilon_\nu)\delta_{\mu\nu} + (\bar{\mu}\mu|\nu\bar{\nu}) - (\nu\mu|\bar{\mu}\bar{\nu}); \\ B_{\mu\nu} &= (\mu\bar{\mu}|\nu\bar{\nu}) - (\mu\bar{\nu}|\nu\bar{\mu}). \end{aligned} \tag{4.15}$$

Here we use the Mulliken notation

$$(\mu\nu|\lambda\kappa) = \int dx_1\, dx_2\; g_{12}\psi_\mu^*(x_1)\psi_\nu(x_1)\psi_\lambda^*(x_2)\psi_\kappa(x_2), \tag{4.16}$$

for the two electron integrals, and the orbital energies are defined by

$$\begin{aligned} \varepsilon_\mu &= \int \psi_\mu^*(x_1)\mathcal{H}_{\text{eff}}(1)\psi_\mu(x_1)\,dx_1; \\ \bar{\varepsilon}_\mu &= \int \bar{\psi}_\mu^*(x_1)\mathcal{H}_{\text{eff}}(1)\bar{\psi}_\mu(x_1)\,dx_1. \end{aligned} \tag{4.17}$$

A matrix with the elements $A_{\mu\nu}$ is self-adjoint,

$$\mathbf{A}^\dagger = \mathbf{A}. \tag{4.18}$$

To complete the definition of the matrix $\mathbf{B}$ we write

$$B_{\mu\nu} = \begin{cases} B_{\nu\mu}; & \mu > \nu; \\ 0; & \mu = \nu, \end{cases} \tag{4.19}$$

which implies that $\mathbf{B}$ is symmetric,

$$\tilde{\mathbf{B}} = \mathbf{B}. \tag{4.20}$$

In general $\mathbf{B}$ is not self-adjoint, though.

In order to write $\delta^2 E$ as a quadratic form involving a self-adjoint matrix we introduce the $2N \times 2N$ matrix

$$\mathbf{T} = \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix}, \tag{4.21}$$

which is self-adjoint, and a column matrix

$$\mathbf{d} = \frac{1}{\sqrt{2}} \begin{bmatrix} \mathbf{c} \\ \mathbf{c}^* \end{bmatrix}, \tag{4.22}$$

where

$$\mathbf{c} = \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_\mu \\ \vdots \\ c_N \end{bmatrix} \tag{4.23}$$

One then gets

$$\delta^2 E = \mathbf{d}^\dagger \mathbf{T} \mathbf{d}. \tag{4.24}$$

Since $\mathbf{T}$ is self-adjoint it can be diagonalized,

$$\mathbf{U}^\dagger\mathbf{T}\mathbf{U} = \mathbf{t} = \begin{bmatrix} t_1 & & & \\ & t_2 & & \\ & & \ddots & \\ & & & t_{2N} \end{bmatrix}, \tag{4.25}$$

which implies that the second variation can be written as

$$\delta^2 E = \mathbf{d}^\dagger\mathbf{U}\mathbf{t}\mathbf{U}^\dagger\mathbf{d} = \sum_{\nu=1}^{2N} t_\nu |e_\nu|^2, \tag{4.26}$$

with

$$\mathbf{e} = \mathbf{U}^\dagger\mathbf{d}. \tag{4.27}$$

Thus if **T** has at least one negative eigenvalue we can choose a set of coefficients c_μ so as to make the second variation negative. Expressed in another way this means that the extremum defined by (4.10) is *unstable* if the matrix **T** is *not* positive definite. In order to show that the extremum is stable one would have to prove that **T** is positive definite for *all* sets of spin orbitals $\{\bar{\psi}_\mu\}$. This is a very difficult problem. It is easy, on the other hand, for a given set $\{\bar{\psi}_\mu\}$ to find the eigenvalues of **T** and thus to find out whether that set can lead to an instability.

In order to simplify this problem further we write the complex quantities **A**, **B**, and **c** in terms of their real and imaginary parts

$$\mathbf{A} = \mathbf{A}_1 + i\mathbf{A}_2; \qquad \mathbf{B} = \mathbf{B}_1 + i\mathbf{B}_2, \tag{4.28}$$

$$\mathbf{c} = \mathbf{a} + i\mathbf{b}. \tag{4.29}$$

From (4.18, 4.20) and (4.28) we get

$$\begin{aligned} \mathbf{A}_1^\dagger &= \mathbf{A}_1; & \mathbf{A}_2^\dagger &= -\mathbf{A}_2; \\ \mathbf{B}_1^\dagger &= \mathbf{B}_1; & \mathbf{B}_2^\dagger &= \mathbf{B}_2. \end{aligned} \tag{4.30}$$

The second variation can then be written

$$\delta^2 E = \bar{\mathbf{d}}^\dagger\bar{\mathbf{T}}\bar{\mathbf{d}}, \tag{4.31}$$

where

$$\bar{\mathbf{d}} = \begin{bmatrix} \mathbf{a} \\ \mathbf{b} \end{bmatrix};$$

$$\bar{\mathbf{T}} = \begin{bmatrix} \mathbf{A}_1 + \mathbf{B}_1 & -\mathbf{A}_2 + \mathbf{B}_2 \\ \mathbf{A}_2 + \mathbf{B}_2 & \mathbf{A}_1 - \mathbf{B}_1 \end{bmatrix}. \tag{4.32}$$

The general problem thus involves a matrix of order $2N \times 2N$. If we restrict the coefficients c_μ to be real we have $\mathbf{b} = 0$, and

$$\delta^2 E = \tilde{\mathbf{a}}(\mathbf{A}_1 + \mathbf{B}_1)\mathbf{a}. \tag{4.33}$$

Similarly if the c_μ are all purely imaginary we have

$$\delta^2 E = \tilde{\mathbf{b}}(\mathbf{A}_1 - \mathbf{B}_1)\mathbf{b}. \tag{4.34}$$

In these two special cases the problem has thus been reduced to the diagonalization of a matrix of order $N \times N$.

The forms (4.25) and (4.32–4.34) of the second variation refer to the spin orbital level. In investigating possible instabilities we always choose a particular set $\{\bar{\psi}_\mu\}$. The corresponding set $\{\phi_\mu\}$ then belongs to the same Fukutome class as the set $\{\psi_\mu\}$ of the reference determinant or to a different one. In either case this type of information can be used to simplify the second variation further.[17] The most well-known examples are the singlet and triplet instabilities of Paldus and Cizek.[24] In the first case the set $\{\phi_\mu\}$ is doubly filled and real and therefore belongs to the Fukutome class TICS like the set $\{\psi_\mu\}$. As we have seen in (4.33), the fact that the spin orbitals are real reduces the matrix $\bar{\mathbf{T}}$ from $2N \times 2N$ to $N \times N$. The fact that the orbitals are doubly filled reduces it further to $(N/2) \times (N/2)$. A similar reduction (but for another reason) occurs when we go from RHF to the Fukutome class ASDW.[17] This provides an example of a triplet (or rather a nonsinglet) instability.

Although we restrict outselves in this article to the Hartree–Fock spin orbitals, it should be mentioned that Paldus and Cizek have also discussed the stability of Brueckner orbitals.[24]

V. Gap Equations

The stability analysis described in the previous section provides a very valuable diagnostic tool for investigating the "phase diagram" for different types of solutions of the GHF equations. For a given system one can expect the character of the solution to depend on a set of parameters characterizing the system: internuclear separations and the nuclear geometry in general, various types of parameters defined by the approximations used, etc. A complete solution of the GHF equations would entail a "phase diagram," indicating for each region which type of solution has the lowest energy. The stability analysis is the appropriate tool for finding the border lines (surfaces) between these regions.

If one has found an instability, other procedures are, however, needed in order to construct explicitly a solution of the "new" type. Obviously there is a large choice of methods for that purpose. There is, however, one which is based on the concept of pairing described in Section III, and which constitutes, as it were, the natural continuation of the stability analysis described in Section IV. It does not at all presuppose a stability analysis, but can be applied directly. It starts out from a representation of the unknown spin orbitals as pairs of spin orbitals of RHF type and from the orthogonal complement of the occupied RHF spin orbitals (3.3). The procedure to be described here is aimed particularly at extended systems, for which the number of variational parameters gets very large. Nothing prevents one, however, from using the same type of procedure for molecular problems.[26]

In Section VII we discuss the use of gap equations in methods going beyond GHF. In this section, however, the total function is a single determinant,

$$D' = \frac{1}{\sqrt{N!}} \det\{\phi_\mu(x)\}, \tag{5.1}$$

with a Fock–Dirac density matrix which we now write in the form (4.3). We assume that a set of partners $\{\bar{\psi}_\mu(x)\}_1^N$, including phases, have been chosen, so that the u_μ and the v_μ are real. An effective one-electron Hamiltonian,

$$\mathcal{H}'_{\text{eff}}(1) = h_1 + \int dx_2\, g_{12}(1 - P_{12})\rho'(x_2, x_2'), \tag{5.2}$$

is associated with D'.

The optimal mixing parameters u_μ are found by minimizing the total energy (2.29) of the function D'. This leads to a set of N coupled equations, which can be put in the form[21]

$$\frac{\partial E'}{\partial u_\mu} = \int dx_1\, \mathcal{H}'_{\text{eff}}(1) \frac{\partial \rho'(x_1, x_1')}{\partial u_\mu} = 0; \qquad \mu = 1, 2, \ldots, N. \tag{5.3}$$

We define a *gap function* $\Delta_\mu = \Delta(\mu)$,

$$\Delta_\mu = -\int dx_1\, \mathcal{H}'_{\text{eff}}(1)\sigma_\mu(x_1, x_1'), \tag{5.4}$$

and an energy difference

$$e_\mu = \int dx_1\, \mathcal{H}'_{\text{eff}}(1)\tau_\mu(x_1, x_1'). \tag{5.5}$$

The reason for the term "gap function" is seen if we regard the calculation of the "new" orbital energies,

$$\varepsilon_\mu = \int dx_1\, \phi_\mu^*(x_1)\mathcal{H}'_{\text{eff}}(1)\phi_\mu(x_1), \tag{5.6}$$

as an expansion problem with the basis ψ_μ, $\bar{\psi}_\mu$. This gives[27]

$$\varepsilon_\mu = \frac{1}{2}\{\epsilon'_\mu + \bar{\epsilon}'_\mu \pm \sqrt{e_\mu^2 + \Delta_\mu^2}\}, \tag{5.7}$$

where

$$\begin{aligned} \epsilon'_\mu &= \int dx_1\, \psi_\mu^*(x_1)\mathcal{H}'_{\text{eff}}(1)\psi_\mu(x_1); \\ \bar{\epsilon}'_\mu &= \int dx_1\, \bar{\psi}_\mu^*(x_1)\mathcal{H}'_{\text{eff}}(1)\bar{\psi}_\mu(x_1). \end{aligned} \tag{5.8}$$

We have

$$e_\mu = \bar{\epsilon}'_\mu - \epsilon'_\mu, \tag{5.9}$$

and the quantity Δ_μ plays the role of a gap in the spectrum.

The extremum conditions (5.3) can be expressed in terms of Δ_μ, e_μ, and the parameter

$$\lambda_\mu = u_\mu^2 - v_\mu^2, \tag{5.10}$$

as

$$e_\mu = (\lambda_\mu/\sqrt{1 - \lambda_\mu^2})\, \Delta_\mu. \tag{5.11}$$

We solve (5.11) for λ_μ,

$$\lambda_\mu = e_\mu/\sqrt{e_\mu^2 + \Delta_\mu^2}, \tag{5.12}$$

which enables us to express $\rho'(x, x')$ in terms of e_μ and Δ_μ since

$$u_\mu v_\mu = \tfrac{1}{2}\sqrt{1 - \lambda_\mu^2} = \Delta_\mu/2\sqrt{e_\mu^2 + \Delta_\mu^2}; \tag{5.13}$$

$$v_\mu^2 = \tfrac{1}{2}(1 - \lambda_\mu) = \tfrac{1}{2}(1 - e_\mu/\overline{e_\mu^2 + \Delta_\mu^2}). \tag{5.14}$$

An equation for the gap function is obtained if (5.13) and (5.14) are used in the definition of Δ_μ (5.4):

$$\Delta_\mu = -\frac{1}{2}\sum_{\nu=1}^{N}\left\{\frac{J_{\mu\nu}\Delta_\nu}{\sqrt{e_\nu^2 + \Delta_\nu^2}} + K_{\mu\nu}\left[1 - \frac{e_\nu}{\sqrt{e_\nu^2 + \Delta_\nu^2}}\right]\right\}, \tag{5.15}$$

where

$$\begin{aligned} J_{\mu\nu} &= \int dx_1\, dx_2\, g_{12}(1 - P_{12})\sigma_\mu(x_1, x_1')\sigma_\nu(x_2, x_2'); \\ K_{\mu\nu} &= \int dx_1\, dx_2\, g_{12}(1 - P_{12})\sigma_\mu(x_1, x_1')\tau_\nu(x_2, x_2'). \end{aligned} \tag{5.16}$$

We notice that the gap equation (5.15) always has the trivial solution $\Delta_\mu = 0$, all μ. The interesting question is whether it also has a nontrivial solution.

Similarly, we get an equation for e_μ by combining the definition (5.5) with (5.13 and 5.14):

$$e_\mu = \bar{\varepsilon}_\mu - \varepsilon_\mu + \frac{1}{2}\sum_{\nu=1}^{N}\left\{\frac{\Delta_\nu K_{\nu\mu}}{\sqrt{e_\nu^2 + \Delta_\nu^2}} + \bar{K}_{\mu\nu}\left[1 - \frac{e_\nu}{\sqrt{e_\nu^2 + \Delta_\nu^2}}\right]\right\}, \quad (5.17)$$

where the first two terms are defined in (4.17) and

$$\bar{K}_{\mu\nu} = \int dx_1\, dx_2\, g_{12}(1 - P_{12})\tau_\mu(x_1, x_1')\tau_\nu(x_2, x_2') \quad (5.18)$$

Orbital forms of (5.15) and (5.17) are obtained when the spin orbital structure of ψ_μ and $\bar{\psi}_\mu$ is used. This normally leads to important simplifications.[17]

These two coupled "integral equations" can be solved iteratively. When the functions Δ_μ and e_μ are known we also know λ_μ from (5.12) and the orbital coefficients

$$\begin{aligned} u_\mu &= \sqrt{\tfrac{1}{2}(1 + \lambda_\mu)}; \\ v_\mu &= \sqrt{\tfrac{1}{2}(1 - \lambda_\mu)}. \end{aligned} \quad (5.19)$$

VI. Applications

In this section we will illustrate the gap concept by some *explicit* applications. We exclude applications to small molecules as well as spin-polarized band calculations, which fall outside the scope of this article. Several of the examples to be discussed are related to the concepts of Mott and Peierls gaps,[21,28] but we will not discuss these very interesting aspects here. A number of—direct or indirect—applications on polyenes have been carried out; these have been treated in another paper.[29]

What remains are calculations for certain model systems: fermion gases in different dimensions and with different types of interactions and the linear chain of hydrogen atoms. These have the advantage that the calculations can be carried out without approximations. They can therefore serve as benchmarks for further work.

The first explicit use of a gap equation in the type of problems discussed here was in a calculation of total and orbital energies for a linear chain of hydrogen atoms.[30] Berggren and Martino arrived at their gap equation in a way other than the one described here. They studied the H_N chain in the AMO approximation [cf. (3.1)], which means that their spin orbitals belong to the Fukutome class ASDW. The pairing partners $\bar{\psi}_\mu$ were taken from the unoccupied part of the band, the lower half of which is doubly filled in RHF. The pairing was vertical in the sense of a band diagram: the wave vectors of ψ_μ and $\bar{\psi}_\mu$ differed by half a Brillouin zone according to the ordinary AMO recipe. The gap equation was solved for five internuclear distances. The results showed as expected that states near the Fermi energy couple more strongly than those far from it, in particular for small internuclear distances.

Another calculation[20] for H_N had a similar goal but was carried out in a different way. Instead of solving a gap equation the authors minimized the total energy directly with respect to a finite but representative number of mixing parameters. The integrals used had also been obtained by procedures other than those used by Berggren and Martino. It is therefore very satisfactory that the results of the two calculations agree very well. The paper by André *et al.* also included a study of certain broken symmetry solutions and a direct UHF calculation, the result of which agrees perfectly with the AMO solution, which must therefore be described as a very good approximation to the GHF solution of ASDW type for H_N.

There is one case in which it has been possible to compare an AMO solution with the *exact* result. This is the linear chain in the Hubbard approximation, for which Lieb and Wu have found the exact solution.[31] Johansson and Berggren[32] studied this problem both with one AMO mixing parameter and with one parameter per pair. They actually carried out their calculations for a spin density wave (SDW) state, but they also showed that for the particular system studied here, an SDW state is equivalent to a multiparameter AMO state. Their gap equation has nontrivial solutions for all densities, although the effect on the total energy gets very small for high densities. The AMO state and the exact solution both have "antiferromagnetic" character. We also note that Misurkin and Ovchinnikov[33] have used the same Hubbard Hamiltonian in a DODS treatment of a polyene.

The fermion gas with δ-function interactions has been treated in three dimensions by Berggren and Johansson[34] and in one dimension by Sykja and Calais.[35] Several Fukutome classes were investigated.

A complete multiparameter AMO calculation has recently been carried out for the three-dimensional electron gas.[36] The unknown mixing parameters u_k and v_k were expanded in cubic harmonics and the corresponding coefficients were found variationally. The results are thus equivalent to the solution of the gap equation. This calculation by Jones and Trickey is an extension of the one-parameter AMO treatment of the electron gas by Laskowski *et al.*[37] In this connection we also recall Overhauser's "instability result": the RHF function for the electron gas is unstable with respect to an SDW state.[38]

In the case of a one-dimensional Coulomb gas the gap equation has been solved for the Fukutome class CCW.[39] There the RHF orbital energy is singular at the Fermi momentum k_f and it is not surprising that the gap function (5.4) and the energy difference (5.5) behave similarly for k near k_f. For high densities the gap vanishes except very near k_f, but for low densities the gap equation has a nontrivial solution for all k.

VII. Beyond the Single-Determinant Approximation

A single determinant with even the most general types of spin orbitals can at best describe certain kinds of correlation. It is always desirable to be able—at least in principle—to improve a given approximation in a systematic way. The concepts and procedures discussed in the previous sections form a very interesting starting point for going beyond the GHF model, in particular, in two directions.

The Hartree–Fock–Bogoliubov (HFB) method[40] contains as one ingredient a generalization of the pairing procedure described in Section III. There *one* RHF spin orbital was paired with *one* function from the orthogonal complement of the occupied spin orbitals. In HFB one creates quasi-particles—bogoliubons—which are mixtures of all occupied and all virtual spin orbitals. The total HFB function is by no means a single determinant, but a mixutre of determinants for different numbers of particles. The amount of pairing in HFB is determined variationally—a further similarity with the use of a gap equation to obtain solutions of the GHF equations.

The HFB state describes a situation in which the number of particles is not fixed. As shown by Weiner and Goscinski,[41] an HFB state can be written as a linear combination of antisymmetrized geminal power (AGP) states for systems with 0, 2, 4, 6, . . . particles. Consequently one can project out of an HFB state the component corresponding to the number of particles of the system under consideration.

The fact that the AMO function is a special case of AGP[42] makes it attractive to think of AGP as one possible next step after GHF. Expressed in CI terminology, AGP constitutes a CI with a huge number of configurations. The calculations can be carried out, though, since by taking advantage of the formal properties of an AGP function one can reduce the number of variational parameters to a manageable size. There is a certain similarity in this respect between AMO and AGP, which is promising for the application of AGP to extended systems.

The coupled-cluster method (CC) is another very promising procedure for constructing correlated wave functions in a systematic way.[43] Unlike CI, CC can be used also for extended systems.[44] A remarkable example of its efficiency is provided by applications to the electron gas for both high, medium, and low densities.[45] In the application of CC methods to extended systems it is essential to use an optimized framework. The reference function is normally chosen as an RHF determinant. This may be the best choice for those values of the parameters characterizing the system, which give RHF (TICS) as the best GHF functions. For other values—for example, the low-density electron gas—another Fukutome class of GHF may have the lowest energy, and then it would seem natural to choose that as a reference function for a CC calculation. Another perhaps even more important decision to be made is the choice of proper basis functions, so as to minimize the computational work. GHF should be able to provide clues and general ideas for both these problems, which ought to be valuable for CC calculations.

In conclusion we should like to propose that the GHF approximation be applied to a number of extended systems, primarily to explore in a systematic fashion what it can do and what it cannot. This will be valuable in its own right, but hopefully also as a preparation for more accurate treatments of the electronic structure of extended systems.

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Electronic Structure of Conductive Conjugated Systems and Their Physicochemical Properties

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I. Introduction

It is certain that electrically conductive polymers have attracted much attention in the field of solid state science in recent years. They are expected to have convenient function in the production of useful electric or electronic devices such as the electrodes in rechargeable batteries, pn-junctions for use in integrated circuits (ICs) or in photovoltaic devices, and so on. In the normal sense, the organic polymers, even the π-conjugated systems having mobile π electrons, are typical insulators of poor electrical conductivity and have been utilized as dielectric material. This is considered to be a result of the Peierls transition (Peierls, 1955), namely, a metallic-insulator transition, e.g., for polyacetylene, which is characteristic in the one-dimensional system. This situation is circumvented by the doping technique, in which the electron acceptors or donors

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are intentionally doped to yield a finite density of states at the Fermi level of the system.

Quantum-chemical treatment of these systems is indispensable for discussing the conduction mechanism based on the electronic structure of the polymers concerned with their physicochemical properties and, furthermore, for providing us with guidelines to design novel, conductive polymers or even superconductors.

As the title of this article suggests, the material covered will deal with the electronic structure of conductive conjugated polymers in relation to their physicochemical properties. This subject is so broad that the theme is confined herein to polyacetylene and other conjugated systems having aromatic rings. The research in this area, however, is rapidly developing and, on reflection, yielding fruitful results that have wide applications and ramifications in quantum chemistry.

II. Polyacetylene

Polyacetylene $(CH)_x$ is one of the simplest conjugated organic polymers. A number of quantum-chemical calculations with respect to the electronic structure of this substance have been accumulated up to the present. There can be distinguished two geometrical isomers of $(CH)_x$ chains, namely, trans and cis. The trans- and cis-type chains are further classified into two and three structural isomers, respectively, in terms of the relative position of the C═C bonds.

Early quantum-chemical studies focused on the findings of the stability of structures (a) and (b) in Fig. 1 (Lennard-Jones, 1937; Coulson, 1939; Ooshika, 1957a,b; Longuet-Higgins and Salem, 1959). This used to be rather an interesting problem since $(CH)_x$ would show metallic property due to the symmetry requirement on its band structure, if it were in the isomeric form of structure (b).

It is now definitely concluded from analyses of Raman scattering spectra (Shirakawa *et al.*, 1973) and X-ray scattering data (Fincher *et al.*, 1982) that the *trans*-$(CH)_x$ has the bond alternant structure (a). The existence of the bond alternation in the *trans*-$(CH)_x$ has also been predicted in terms of the Peierls transition from early work in the field of solid state physics (Peierls, 1955).

Two decades ago, Little (1964) pointed out the possibility of high-temperature superconductivity ($T_c \approx 2200$ K) in the polyene chain, of which some portion of the hydrogen atoms is appropriately substituted by dye molecules such as diethylcyanine iodide. This proposal has been controversial (Paulus, 1966; Salem, 1966; Little, 1967) and there has been no embodiment synthesized based on this idea.

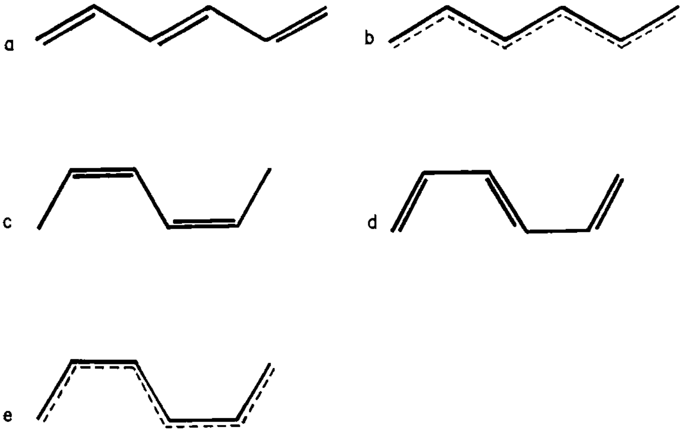


Fig. 1. Geometrical and structural isomers of $(CH)_x$; (a) trans-transoid, (b) trans-regular, (c) cis-transoid, (d) trans-cisoid, and (e) cis-regular.

The curtain of the epoch-making event to this end rose without doubt when a dramatic increase was observed in the electrical conductivity of a highly crystalline film of $(CH)_x$ doped with electron acceptors or donors (Shirakawa *et al.*, 1977; Chiang *et al.*, 1977, 1978). The $(CH)_x$ film used for this purpose is prepared by what is called Shirakawa's method based on the use of a Ziegler catalyst of a high concentration (Ito *et al.*, 1974; Shirakawa and Ikeda, 1979/1980). A great number of experimental and theoretical investigations on pristine and doped $(CH)_x$ have been undertaken since the discovery described above (MacDiarmid and Heeger, 1979; Heeger and MacDiarmid, 1980). In this article we hope simply to describe the electronic structure of $(CH)_x$ and try to interpret some of its fundamental physicochemical properties by way of analysis of the electronic structure. Methodology of quantum-chemical calculations of polymers including $(CH)_x$ has been discussed by Kertész (1982), and details on this theme will not be described here.

A. Electronic Structure of *Cis*- and *Trans*-Polyacetylene

The electronic structure of $(CH)_x$ has been studied using various approaches within the framework of the one-dimensional tight-binding crystal orbital (CO) method, that is, from the Hückel to the *ab initio* Hartree–Fock level (see, e.g., Kertész, 1982). Some of the calculated results of the energetic stability of the $(CH)_x$ isomers in Fig. 1 are listed in Table I.

It has been concluded from these calculated results that the *trans*-$(CH)_x$ is more stable than the *cis*-$(CH)_x$, in agreement with the cis–trans

TABLE I

RELATIVE STABILITIES OF $(CH)_x$ ISOMERS: COMPARISON WITH LITERATURE DATA[a]

Structure	Extended Hückel[b]	CNDO/2[c]	*Ab initio* (STO-3G)[d]
Trans-transoid	0	0	0
Trans-regular	0.04	0.16	0.32
Cis-transoid	0.24	0.07	0.08
Trans-cisoid	0.21	0.17	0.09
Cis-regular	—	0.28	0.31

[a] Energies are given relative to the trans-transoid structure per C_2H_2 unit. All values are in electron volts.

[b] Whangbo *et al.* (1979).

[c] Yamabe *et al.* (1979a,b).

[d] Karpfen and Höller (1981).

thermal isomerization experiment (Ito *et al.*, 1975). Furthermore, the trans-transoid skeleton is more stable than the trans-regular, which has also been proved by X-ray scattering analyses (Fincher *et al.*, 1982) as well as Raman scattering observations with respect to the C═C and the C—C stretching modes (Shirakawa *et al.*, 1973). These studies have given verification to the occurrence of the Peierls transition in the long-chain polyene, introducing the band gap dependent on the degree of bond alternation in the trans-transoid chain. This also implies that the electronic correlation (Ovchinikov *et al.*, 1973) does not play a crucial role in the determination of the band gap of $(CH)_x$.

On the other hand, of *cis*-$(CH)_x$ isomers, the calculation favors the cis-transoid skeleton over the other two, corresponding to the suggestion by the Raman spectral result of Shirakawa *et al.* (1973). Hence, in this article, we simply term the trans-transoid and the cis-transoid $(CH)_x$ as the *trans*- and the *cis*-$(CH)_x$, respectively, unless specially noted. We shall analyze the electronic structure of the *trans*- and *cis*-$(CH)_x$ qualitatively based on the CNDO/2 results by Yamabe *et al.* (1979a,b) in the following discussion.

In Fig. 2 are depicted the interatomic interaction energies and the π bond orders (in parentheses) in the two isomers of $(CH)_x$. Both the interatomic interaction energies and the π bond orders signify that *cis*-$(CH)_x$ has the stronger C═C bonds and that the trans isomer has the stronger C—C bonds. These tendencies well explain the observations of the Raman scattering spectra listed in Table II. It is of interest to note that C_1 and C_4 in *cis*-$(CH)_x$ are repulsive, which seems to relate with the fact the angle $C_1C_2C_3$ is not 120° but approximately 127° (Baughman *et al.*, 1978; Karpfen and Höller, 1981). The repulsive interaction between H_6 and H_7

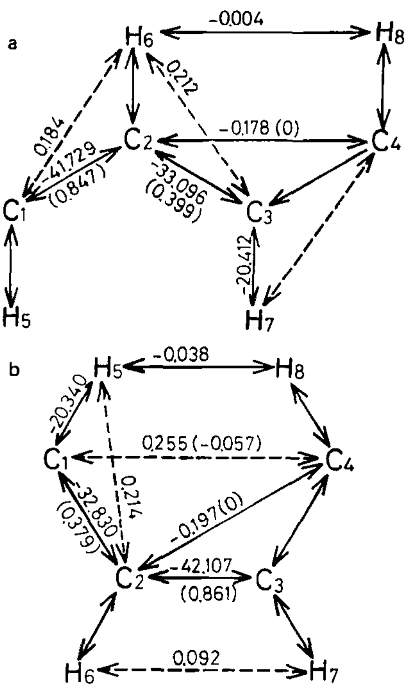


Fig. 2. Interatomic interaction energies in (a) *trans*-$(CH)_x$ and (b) *cis*-$(CH)_x$. The positive and the negative values in electron volts signify the repulsive and the attractive interactions, respectively. Values in parentheses are π bond order.

in *cis*-$(CH)_x$ exceeds the attraction between H_5 and H_8, which determines that *cis*-$(CH)_x$ is less energetically stable than *trans*-$(CH)_x$ in total.

It should be noted here that the cis-regular $(CH)_x$ (Fig. 1e) has a finite band gap apart from the trans-regular (Fig. 1b) (Yamabe *et al.*, 1979a). This is due to the difference of the symmetries of these two structures.

TABLE II

RAMAN LINES OF THE C=C AND THE C—C STRETCHINGS OF *TRANS*- AND *CIS*-$(CH)_x$[a]

	Trans-$(CH)_x$		*Cis*-$(CH)_x$	
C=C	1470 (1474)[b]	A_g	1544 (1552)	A_g
C—C	1090–1120 (1080)	A_g	915 (920)	B_{2g}

[a] Values in cm^{-1}. From Kuzmany (1980).

[b] Values in parentheses are due to Shirakawa *et al.* (1973).

That is, a polymer having degeneracy of the highest occupied (HO) and the lowest unoccupied (LU) bands becomes continuous in the Brillouin zone, which makes this polymer metallic. The cis-regular $(CH)_x$ has the unit cell consisting of C_2H_2, and the trans-regular, of CH. Hence the unit cells of the cis-regular and the trans-regular $(CH)_x$ have even and odd numbers of π electrons, respectively.

Usual crystal orbitals extend all over the system concerned and are obtained so as to fulfill the Bloch theorem (Bloch, 1928). However, it is known to be rather useful to convert the wave function of the system into the localized function for the purpose of the discussion of the local nature of the system, such as the exciton. One such function is the Wannier function a_p derived by the Fourier transformation of the crystal orbital Φ_p,

$$a_p(\mathbf{r} - j\mathbf{a}) \equiv \frac{1}{\sqrt{2N+1}} \sum_{k}^{\mathrm{BZ}} \exp(-i\mathbf{k} \cdot j\mathbf{a})\Phi_p(\mathbf{k}, \mathbf{r}) \qquad (j = 0, \pm 1, \pm 2, \ldots, \pm N) \tag{1}$$

where p is the level of the Wannier function centered at the jth cell, $\mathbf{k}$ is the wave number, $\mathbf{a}$ is the unit vector of translational symmetry, BZ represents the summation over the Brillouin zone, and $2N + 1$ is the number of unit cells (Wannier, 1937). The occupied and the unoccupied Wannier functions of the trans-regular $(CH)_x$ at the zeroth cell have been obtained analytically within the framework of the Hückel Hamiltonian (Tanaka *et al.*, 1977) as

$$\begin{aligned} a_1(\mathbf{r}) &= \sum_{j=0}^{\pm N} \frac{1}{2\pi} \left[\frac{\sqrt{2}\sin(j\pi)}{j} \chi_1(\mathbf{r} - j\mathbf{a}) + \frac{\sqrt{2}\sin\{(j + 1/2)\pi\}}{j + 1/2} \chi_2(\mathbf{r} - \{j + 1/2\}\mathbf{a}) \right] \\ a_2(\mathbf{r}) &= \sum_{j=0}^{\pm N} \frac{1}{2\pi} \left[\frac{\sqrt{2}\sin(j\pi)}{j} \chi_1(\mathbf{r} - j\mathbf{a}) - \frac{\sqrt{2}\sin\{(j + 1/2)\pi\}}{j + 1/2} \chi_2(\mathbf{r} - \{j + 1/2\}\mathbf{a}) \right] \end{aligned} \tag{2}$$

for the occupied and unoccupied functions, respectively. The orbital patterns of these are illustrated in Fig. 3.

With the use of these localized functions, one can describe the influence on the electronic structure caused by the local perturbations which breaks the symmetry of the whole system. Tanaka *et al.* (1977) have examined (1) the case in which a carbon atom in the infinite chain is

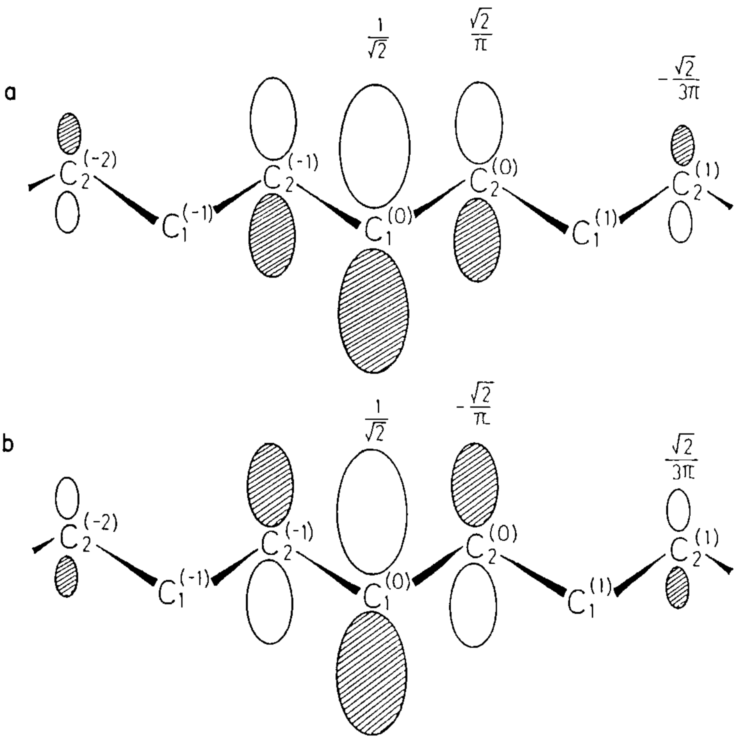


Fig. 3. Orbital patterns of the Wannier functions; (a) $a_1(\mathbf{r})$ and (b) $a_2(\mathbf{r})$.

replaced by another atom X, (2) the case in which one of the bond lengths in the chain is changed, and (3) the case in which the infinite polyene is perturbed by another carbon atom through a weak bond formation. The treatment mentioned here will be easily extended to the *trans*-$(CH)_x$ perturbed by a dopant such as iodine or AsF_5, where the charge transfer between the $(CH)_x$ and the dopants occurs introducing the decrease of the π bond orders and the formation of the dipole moments around the perturbed carbon atoms. In order to describe the Wannier functions of the *trans*-$(CH)_x$, that is, of the bond alternant chains, one may use approximate functions defined as

$$\begin{aligned} A_1(\mathbf{r}-j\mathbf{a}) &\equiv \frac{1}{\sqrt{2}}\left[a_1(\mathbf{r}-j\mathbf{a}) + a_1(\mathbf{r}-\{j+1/2\}\mathbf{a})\right] \qquad \text{(occupied)} \\ A_2(\mathbf{r}-j\mathbf{a}) &\equiv \frac{1}{\sqrt{2}}\left[a_2(\mathbf{r}-j\mathbf{a}) - a_2(\mathbf{r}-\{j+1/2\}\mathbf{a})\right] \qquad \text{(unoccupied)} \end{aligned} \tag{3}$$

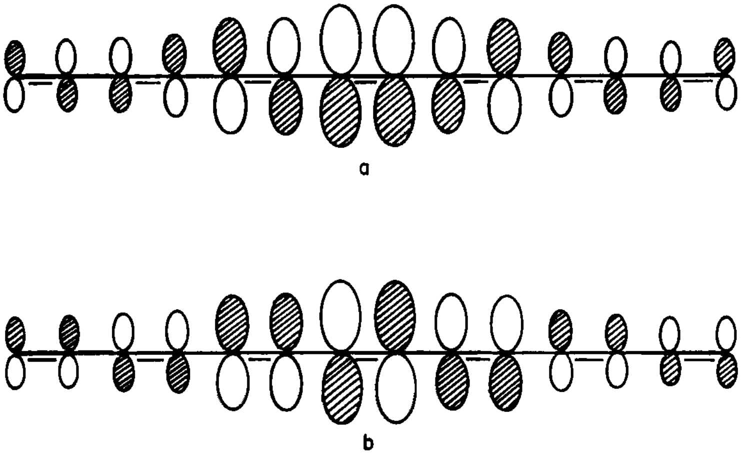


Fig. 4. Orbital patterns of the Wannier functions with the bond alternation; (a) $A_1(\mathbf{r})$ and (b) $A_2(\mathbf{r})$.

The orbital patterns of these are shown in Fig. 4. The Wannier functions thus obtained are in good agreement with those derived directly from the semiempirical (PPP)-crystal orbitals (Pugh, 1973).

The localization of electrons in a certain random lattice was pointed out by Anderson (1958). The localization problem in the one-dimensional random lattice has been discussed by several authors (Mott and Twose, 1961; Bell and Dean, 1970). It has been proved that the localization is caused by any small deviation of potentials at the lattice points in the one-dimensional system of an infinite chain length (Gol'shtein *et al.*, 1977; Molchanov, 1978). This signifies that any one-dimensional systems will become insulators since one can not expect an actual substance free from infinitesimal deviation of the potentials.

A $(CH)_x$ polymer chain, however, is considered to consist of an array of about 500 carbon atoms (Shirakawa *et al.*, 1980), which may reduce the localization "syndrome" described above. The localization characteristics of the electronic wave function have been studied with respect to the $(CH)_x$ model consisting of 300 carbon atoms with the diagonal of the off-diagonal disorder of the potentials (Tanaka *et al.*, 1983a). The results have shown that the eigenfunction near the Fermi level is relatively "strong" against the temptation to localize caused by the existence of the random potentials.

B. Cis-to-Trans Isomerization

As has been stated above, the *trans*-$(CH)_x$ is thermodynamically more stable than the cis isomer, and hence the latter isomerizes irreversibly to the former by the thermal processing (Ito *et al.*, 1975). The study of the isomerization is crucial when handling a $(CH)_x$ polymer, since the structure of the as-polymerized $(CH)_x$ is of cis type due to the cis opening of the triple bonds of acetylene during the polymerization reaction (Shirakawa and Ikeda, 1971). It has been known that the doping process involving the *cis*-$(CH)_x$ or irradiation of the *cis*-$(CH)_x$ with light having appropriate photon energy also brings about the isomerization (Fincher *et al.*, 1979b; Tanaka *et al.*, 1983b,c).

However, the mechanism of this irreversible isomerization process has not been fully rationalized up to the present. In this section a quantum-chemical approach for the understanding of this process is discussed (Yamabe *et al.*, 1981, 1982a).

Assuming that the internal rotation inducing the thermal isomerization takes place at any site of $(CH)_x$, two possible mechanisms may be considered, as shown in Fig. 5. The rotational types A and B occur around the C=C and the C—C bonds, respectively. The calculations with respect to the finite polyene $C_{12}H_{14}$ for the model of $(CH)_x$ using the RHF and the UHF MINDO/3 MO method have favored the A-type as a more preferable motion to cause the thermal isomerization, the energy barrier of the rotation being approximately 1.0 eV (Fig. 6). The original bonds $C_3{=}C_4$ and $C_7{=}C_8$ in type A become weakened as the dihedral angle ϕ between the planes of the β unit and the polymer chain increases. When $\phi = 90°$, the occurrence of a biradical nature in the β unit has been suggested, which is usually encountered in the photoisomerization process of linear conjugated polyenes (Bonačić-Koutecký and Ishimaru, 1977). The final geometry ($\phi = 180°$) has been found to be more stable than the initial one ($\phi = 0°$) by 0.56 eV. The rotation probably starts from the surface area of the fibrils consisting of $(CH)_x$ chains. The trans moiety thus formed will have various distribution of the chain lengths. Hence it is expected that the activation energy for the isomerization becomes larger as the isomer-

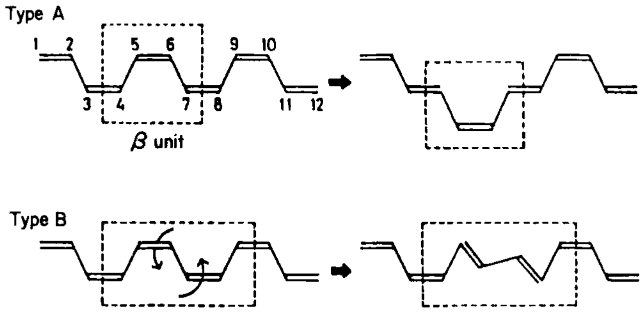
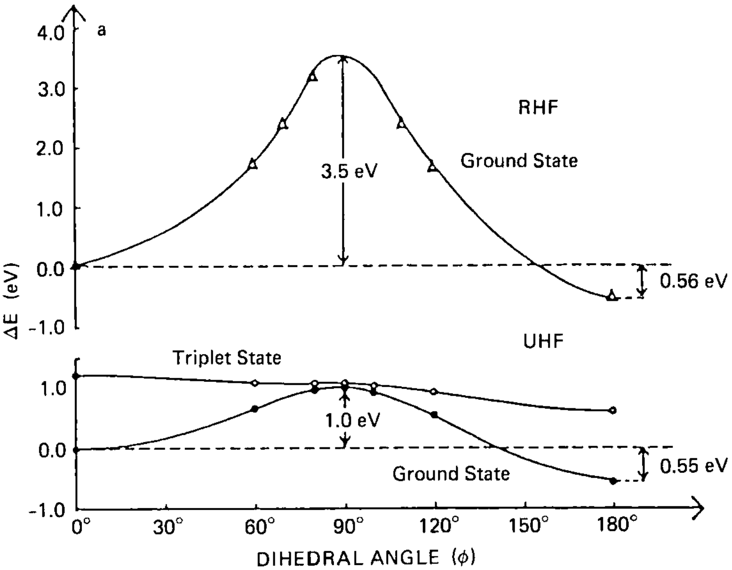


Fig. 5. Two kinds of internal rotations A and B responsible for thermal isomerization.



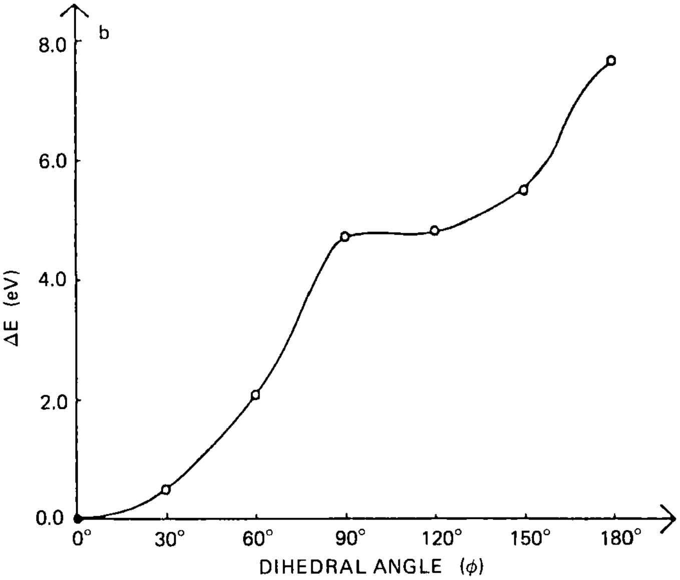


Fig. 6. Potential curves for (a) type A and (b) type B rotations defined in Fig. 5 for the cis-transoid $C_{12}H_{14}$. See text with respect to the definition of dihedral angle.

ization process proceeds, and that the structure of the whole polymer becomes more disordered, which corresponds well to the experimental observation (Ito *et al.*, 1975).

The cis–trans isomerization also caused during the doping process (Tanaka *et al.*, 1983b) has been observed in optical absorption (Fincher *et al.*, 1979b), NMR spectral analysis (Mihály *et al.*, 1979/80), specific heat analysis (Moses *et al.*, 1980), and resonance Raman scattering (Kuzmany, 1980). An interpretation to the mechanism of this kind of isomerization has been elucidated by the representations seen in Fig. 7 (Yamabe *et al.*, 1981). The dopants (e.g., electron acceptors) withdrawing π electrons from the cis polymer skeleton change the original cis-transoid into the trans-cisoid form, which is a form of the excited-state configuration of the cis isomer and is unstable. A successive internal rotation around two C—C bonds of the trans-cisoid chain yields the trans moiety. The largest possible separation of two charged solitons (designated by + signs in Fig. 7c) has been estimated to be approximately 26 Å (Takano, 1983). The

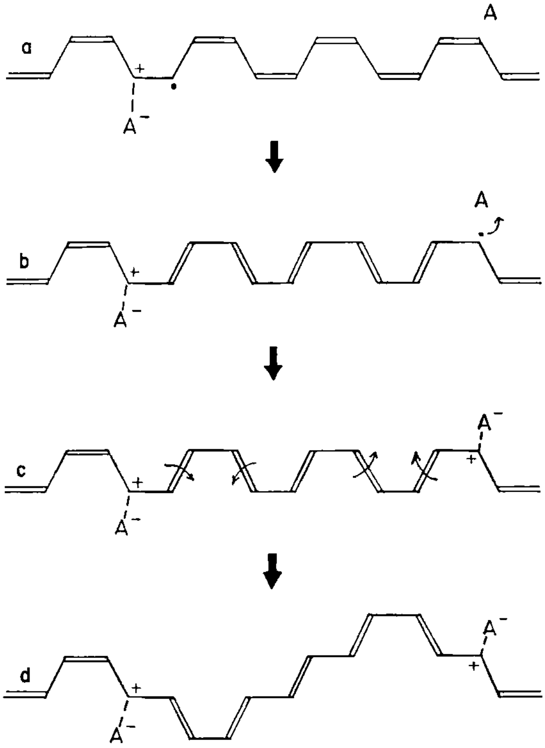


Fig. 7. Mechanism for the electron transfer in the *trans*-$(CH)_x$.

calculated result with respect to a finite trans-cisoid model $C_{20}H_{22}$ using the MINDO/3 MO method has indicated that the rotation of the β unit shown in Fig. 8 is the motion without the barrier, and that the subsequent rotation of the α unit proceeds along the very shallow potential, the depth of which is less than 0.1 eV, as shown in Fig. 9 (Yamabe *et al.*, 1981, 1982a). It is expected that the latter rotation further induces the rotation of the β' unit.

The cis–trans photoisomerization has recenty been confirmed experimentally (Tanaka *et al.*, 1983c) based on the idea that the orbital pattern of the LUMO accompanied by the bottom of the conduction band of the cis isomer favors the trans-cisoid skeleton (Yamabe *et al.*, 1979b). The mechanism of the photoisomerization will be interpreted almost in a similar way to what was discussed for the doping-induced isomerization de-

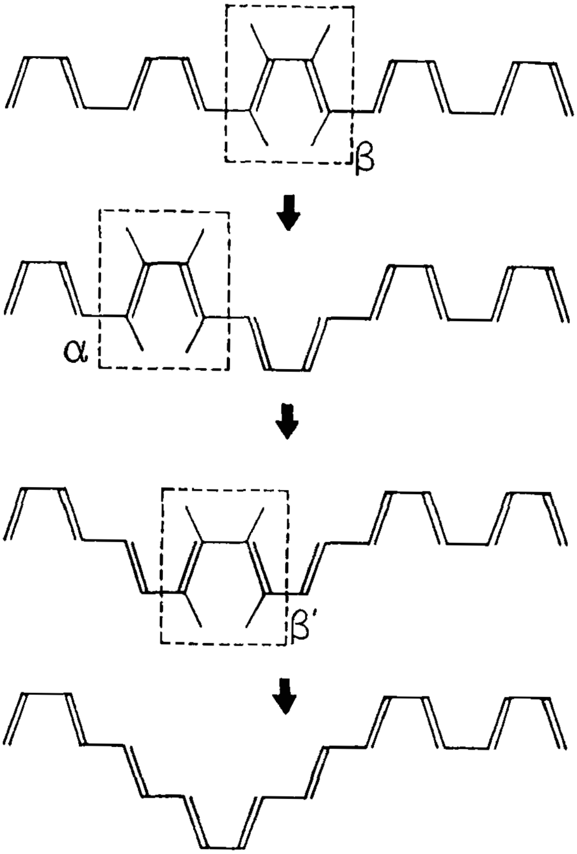


Fig. 8. Rotations of α and β units in trans-cisoid $C_{20}H_{22}$ polyene.

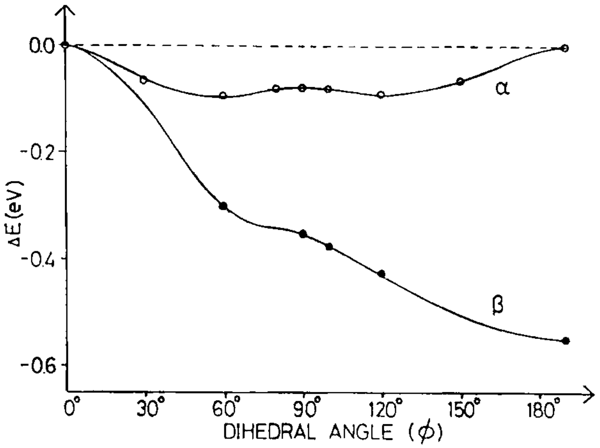


Fig. 9. Potential curves for rotations α and β units in Fig. 8.

scribed above, once the photoinduced trans-cisoid skeleton is formed. It is of interest to note that there can be two kinds of boundaries between the cis-transoid and the trans-cisoid domains, that is, the neutral and charged kinks as shown in Fig. 10. This is still an open question at present, which should be examined in a quantum-chemical approach.

It has also been suggested that photoexcitation of the cis-transoid skeleton with energy corresponding to its optical band gap yields the trans-cisoid moiety (Tanaka *et al.*, 1984a). The growth of four new IR absorption peaks, found after irradiation at 802, 1062, 1112, and 1259 cm^{-1}, was ascribed to the vibrational modes in trans-cisoid $(CH)_x$. Hence, the trans-cisoid structure does not collapse for a considerably long time in the actual $(CH)_x$ polymer, which suggests the existence of a local potential minimum around this structure in the potential hypersurface.

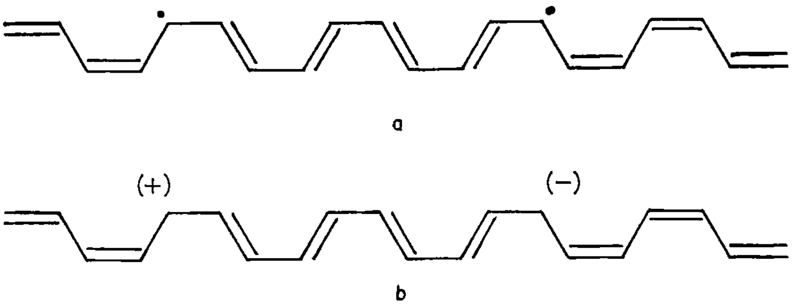


Fig. 10. The boundary between the cis-transoid and the trans-cisoid structure. (a) The neutral and (b) charged kinks.

C. Vibrational Structure

The analysis of $(CH)_x$ in terms of IR and Raman scattering spectroscopy is of fundamental importance in the study of the structure of this polymer, as for usual organic compounds. The *trans*-$(CH)_x$ is isomorphous to the point group C_{2h}, the cis isomer, to D_{2h}. The assignment of IR and Raman scattering spectra has been reported together with that for the deuterized polymer (Shirakawa and Ikeda, 1971; Shirakawa *et al.*, 1973; Kuzmany, 1980).

For the analysis of the spectra of *trans*-$(CH)_x$, valence-force-field calculations have been performed, the force constant being empirically fitted so as to reproduce the observed vibrational frequencies (Inagaki *et al.*, 1975; Schügerl and Kuzmany, 1981). The energy gradient scheme based on the *ab initio* crystal orbital method has also been attempted for the study of the vibrational structure of *trans*- and *cis*-$(CH)_x$ (Teramae *et al.*, 1984). The calculated result of the vibrational frequencies has been found to depend upon the quality of the basis set. It has been demonstrated that, e.g., for the 4-31G basis, a uniform scaling of the force constants, multiplying by 0.8, is required to adjust the vibrational frequencies of the *trans*-$(CH)_x$ (Table III).

The doped $(CH)_x$, with electron acceptor or donor such as AsF_5, I_2, or Na, shows electric conductivity of $10^1 \sim 10^3$ S cm^{-1} (Shirakawa *et al.*, 1977; Chiang *et al.*, 1977, 1978) and, hence, the electromagnetic wave of the frequencies in the IR regime becomes unable to transmit the doped $(CH)_x$ due to the skin effect (e.g., Slater and Frank, 1947). At a slight

TABLE III

CALCULATED RESULTS OF THE VIBRATIONAL FREQUENCIES OF *TRANS*-$(CH)_x$[a]

Symmetry	Calc.[b]	Calc. (scaling)[c]	Experimental[d]	Assignment
A_g	1310	1172	1060	C—C str.
	1460	1306	1285	C—C def. in plane
	1911	1709	1450	C=C str.
	3264	2920	2990	C—H str.
A_u	1149	1028	1015	C—H def. out-of-plane
B_g	1123	1005	1008	C—H def. out-of-plane
B_u	1336	1195	1292	C—H def. in-plane
	3305	2956	3013	C—H a-str.

[a] Values in cm^{-1}.
[b] 4-31G basis set.
[c] 4-31G basis set with scaled force constants.
[d] Shirakawa and Ikeda (1971); Kuzmany (1980).

doping level, an appearance of three new IR bands at 888, 1288, and 1397 cm^{-1}, independent of the dopant species, has been reported (Fincher *et al.*, 1979a; Rabolt *et al.*, 1979; Harada *et al.*, 1980). In addition, a couple of weak bands, such as at 814 and 1177 cm^{-1}, have been observed (Clarke *et al.*, 1982).

The three stronger new bands are sometimes referred to as the soliton vibrations, the nature of which has been controversial. Experimental studies on doped $(\mathrm{CH})_x$ and $(\mathrm{CD})_x$ have confirmed the origin of these bands as arising in the molecular vibrations of the polyene chain. For instance, it has been observed that the bands at 888 and 1397 cm^{-1} shift to lower frequencies for doped $(\mathrm{CD})_x$ (Rabolt *et al.*, 1979). This suggests a possible contribution from the C—H bending mode to these bands. The origin of these doping-induced IR bands has been discussed in terms of the vibronic activation, that is, the enhancement of the totally symmetric Raman-active A_g modes (Rabolt *et al.*, 1979), or in terms of the ungerade vibrations of the positively (or negatively) charged solitons formed in the $(\mathrm{CH})_x$ chain (Harada *et al.*, 1980). The details of the soliton will be described in Section II,E.

There has also been an attempt to elucidate the band origin using an MO calculation of finite cationic polyenes as a model of oxidized $(\mathrm{CH})_x$, the electron loss of which is due to the presence of the dopant (electron acceptor) near the chain (Yamabe *et al.*, 1982b,c). The results have shown that the charge density polarization in the chain generated by the electron loss is responsible for the new IR bands. For instance, the MINDO/3 calculation results with respect to the net charge distribution of $\mathrm{C}_{21}\mathrm{H}_{23}{}^{+}$ species in the optimized geometry are shown in Fig. 11a. This kind of polarization has actually been observed as the chemical shift in the $^{13}\mathrm{C}$ solid state NMR of the doped *trans*-$(\mathrm{CH})_x$ (Terao *et al.*, 1984). In Fig. 11b is also shown the position of the positive charges in $\mathrm{C}_{22}\mathrm{H}_{24}{}^{2+}$, indicating the separation of two charges due to the electrostatic repulsion. On the

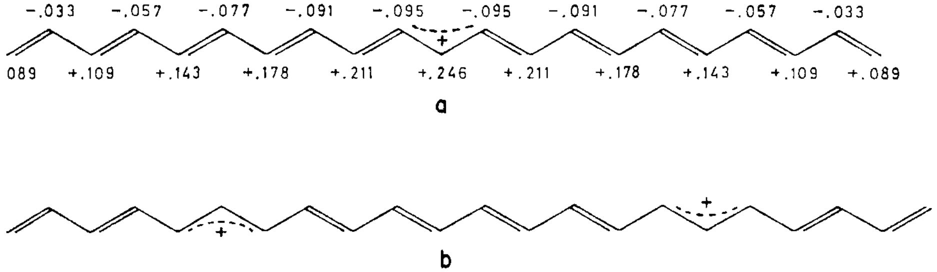


Fig. 11. Analysis of the charge distribution of (a) $\mathrm{C}_{21}\mathrm{H}_{23}{}^{+}$ and (b) $\mathrm{C}_{22}\mathrm{H}_{24}{}^{2+}$.

other hand, an interpretation based on the charged soliton mechanism has also been proposed (Mele and Rice, 1980).

Meanwhile, the IR study on the photoexcited *trans*-$(CH)_x$, in which the excited electron–hole pair is expected to change rapidly (a time of order 10^{-13} sec) into a charged soliton pair (Su and Schrieffer, 1980), has revealed the complete absence of the band around 900 (888) cm^{-1}, the other two bands (1260 and 1370 cm^{-1}) remaining (Blanchet *et al.*, 1983; Vardeny *et al.*, 1983). Hence the doping-induced band at 888 cm^{-1} is currently considered to be due to a pinned mode of dopant-induced carriers in the $(CH)_x$ chain.

D. Photoexcitation

The optical properties of $(CH)_x$ are of interest, since these directly give information about the band gap and/or the levels in the midgap, which is considered to be closely related with the electric transport property. Currently available experimental data on the photoabsorption of $(CH)_x$ polymers are listed in Table IV. It seems to be reasonable to regard these absorption onsets as the $\pi \rightarrow \pi^*$ interband transition energy from the HO to the LU band, that is, the band gap between the valence and the conduction bands in the sense of the one-electron approximation based on the one-dimensional Peierls transition mentioned in the Section II,A.

An additional verification of this interpretation has come from the observed threshold value 1.48 eV for a photovoltaic response of the *trans*-$(CH)_x$ slightly doped with AsF_5 (Tani *et al.*, 1980).

The calculated band gap values by the crystal orbital methods (Kertész *et al.*, 1978; Yamabe *et al.*, 1979a; Suhai, 1980) are rather too large

TABLE IV

PHOTOABSORPTION DATA OF $(CH)_x$[a]

	Trans-$(CH)_x$	*Cis*-$(CH)_x$
Absorption onset[b]	1.4	1.6
	(1.35)[c]	(1.78)
Maximum absorption	1.9	2.1
	(1.77)	(2.09)

[a] Values in electron volts. From Fincher *et al.* (1979b).

[b] The point where the absorption rises up sharply (equal to the optical band gap).

[c] Values in parentheses are due to Shirakawa *et al.* (1973).

TABLE V

THRESHOLD ENERGY VALUES[a] CAUSING PHENOMENA RELATED TO THE PHOTOEXCITATION

	Trans-$(CH)_x$	*Cis*-$(CH)_x$
Photoconductivity[b]	1.0	No such phenomenon
Photoisomerization[c]	No such phenomenon	2.03
Photoluminescence[b]	No such phenomenon	2.05

[a] Values in electron volts.

[b] Lauchlan *et al.* (1981).

[c] Tanaka *et al.* (1983*c*).

[d] The possibility of the photoluminescence in the *trans*-$(CH)_x$ has also been discussed by Yoshino *et al.* (1983).

(7 ~ 9 eV) compared with the experimental values. On the other hand, the values of the interband transition energy obtained from the extrapolation of the finite conjugated polyenes correspond well with the observed values in Table IV. Duke *et al.* (1978) have obtained the value 2.3 eV from the extrapolation for the infinite polyene ($n \rightarrow \infty$) of the $C_{4n}H_{4n+2}$ form employing the semiempirical CNDO/S2 MO method. This treatment has been refined by Yamabe *et al.* (1982d), including all singly excited configuration interactions, where the absorption maximum band of *trans*-$(CH)_x$ has been assigned to the 1 ^1B_u excitation in $C_{2n}H_{2n+2}$ (even polyenes) and possibly to the 2 $^2A_1$ in $C_{2n+1}H_{2n+3}\cdot$ (odd polyenes).

Some other optical properties are listed in Table V. It is to be noted that the threshold value 1.0 eV for the photoconduction in *trans*-$(CH)_x$ is smaller than the band gap of this substance. This discrepancy has been interpreted by invoking charged solitons photogenerated either directly or indirectly through the electron–hole pair as mentioned in Section II,C (Etemad *et al.*, 1981).

When *trans*-$(CH)_x$ is doped with electron acceptors, the intensity of the $\pi \rightarrow \pi^*$ interband transition peak around 1.9 eV decreases and a new peak at 0.7 eV from the top of the valence band appears (Suzuki *et al.*, 1980). This midgap band is currently suspected to stem from the soliton formation in the *trans*-$(CH)_x$ chain. The model calculation employing cationic polyenes of finite length has attributed the absorption band at 0.7 eV to 2 ^2A_u excitation in $C_{2n}H_{2n+2}^{+\cdot}$, 1 $^1B_1$ in $C_{2n+1}H_{2n+3}^{+}$, or 1 ^1B_u in $C_{2n}H_{2n+2}^{2+}$ (Yamabe *et al.*, 1982d). Midgap state calculations for the *trans*-$(CH)_x$ have also been performed in the framework of the Hückel Hamiltonian including the σ-bond compressibility (Brédas *et al.*, 1982a).

The observation of a sharp absorption at 1.47 eV has been reported in the *trans*-$(CH)_x$ with the dilute doping limit and interpreted in terms of the polaron formation (Etemad *et al.*, 1983).

E. Solitons in Polyacetylene and the Mechanism of the High Conductivity of Polyacetylene Derivatives

More than two decades ago Pople and Walmsley (1962) discussed the existence of an unpaired π electron in the *trans*-$(CH)_x$ as shown in Fig. 12a, which accompanies a localized nonbonding MO level. This has been actually confirmed by ESR analyses (Shirakawa *et al.*, 1978) and ENDOR (Kuroda and Shirakawa, 1982) observations. The lineshape of the ESR shows the motional narrowing from a highly mobile π electron in the $(CH)_x$ chain even down to 10 K (Goldberg *et al.*, 1979; Weinberger *et al.*, 1980). It has been concluded that there is one unpaired electron per approximately 3000 carbon atoms. This unpaired π electron in the *trans*-$(CH)_x$ chain is frequently referred to as the bond alternation domain wall, phase kink, or soliton.

The concept of the soliton has been introduced in the theoretical treatment by Su *et al.* (1979, 1980), in which they have employed a model Hamiltonian within the framework of the Hückel approximation, including both σ-bond compressibility and the kinetic energy term of the CH units. The soliton is an elementary excitation and, in the case of the *trans*-$(CH)_x$ in Fig. 12a, is expected to satisfy a wave equation akin to the ψ^4 field theory (Krumhansl and Schrieffer, 1975). The estimated energy of the creation of a soliton is 0.4 eV and the periodic-lattice-induced activation energy for the soliton motion is 0.002 eV, the latter being consistent with the result of the ESR observation. The energy of a soliton is most stabilized when its tail (that is, the spatial halfwidth of the kink) extends over seven carbon sites.

The model Hamiltonian mentioned above has been expanded to the continuum limit so as to characterize the soliton almost analytically (Takayama *et al.*, 1980). In the *cis*-$(CH)_x$, on the other hand, an unpaired

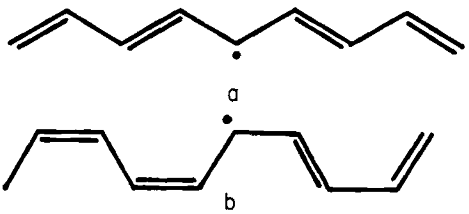


Fig. 12. Neutral kink in (a) *trans*-$(CH)_x$ and (b) *cis*-$(CH)_x$. In the case of the *trans*-$(CH)_x$ it is called a neutral soliton.

TABLE VI

TRANSPORT AND MAGNETIC PROPERTIES OF THE $(CH)_x$ DERIVATIVES AT TYPICAL DOPANT CONCENTRATION REGIMES

Dopant mol%	Electric conductivity[a]	Thermopower[a]	Contribution from Curie-law susceptibility[b]	Contribution from Pauli susceptibility[c]
$0 \sim 0.1$	Rapid increase	Rapid decrease	Rapid decrease	Small
$0.1 \sim 7$	Large	Small	Small	Small
>7	Large	Small	Small	Rapid increase

[a] Moses *et al.* (1982).
[b] Epstein *et al.* (1981).
[c] Ikehata *et al.* (1980).

π electron introduces two different structural phases, that is, the cis-transoid and the trans-cisoid as shown in Fig. 12b, with different energies. Hence unpaired π electrons in the *cis*-$(CH)_x$ are expected to be less stable and spatially more confined. As a matter of fact, no radical spins have been detected by the *in situ* observation for the *cis*-$(CH)_x$ prepared under low temperature (Snow *et al.*, 1979; Chien *et al.*, 1980; Bernier *et al.*, 1980).

When either *cis*- or *trans*-$(CH)_x$ is doped with an appropriate electron acceptor or donor, such as AsF_5, I_2, or Na, the electric conductivity is varied over a range of 11 orders of magnitude up to 10^3 S cm^{-1} through a semiconductor–metal transition according to the dopant concentrations (Shirakawa *et al.*, 1977; Chiang *et al.*, 1977, 1978). The polyacetylene derivative consisting of the $(CH)_x$ and the dopant is considered as a kind of charge-transfer complex manifesting a p-type or n-type property according to the dopant character.

The soliton in the pristine *trans*-$(CH)_x$ as discussed above is neutral and, hence, will not play a role of charge carrier in the $(CH)_x$ derivative. In Table VI are listed the transport and the magnetic properties of the $(CH)_x$ derivatives at typical dopant concentration regimes. The transport properties such as electric conductivity and thermopower indicate the occurrence of the semiconductor–metal transition at 0.1 mol% of the dopant concentration (dilute doping regime). Pauli susceptibility from free carriers, however, remains small until reaching concentrations in excess of 7 mol% (heavily doped regime). On the other hand, there is almost no contribution from the Curie-law susceptibility in the range of $0.1 \sim 7$ mol% (lightly doped regime), suggesting that the charge carriers in this regime are spinless. This anomalous phenomenon, being of "countertraditional sense" in the lightly doped regime, is closely connected with the characteristic structure of the *trans*-$(CH)_x$ and can be elucidated in terms of the soliton doping as follows, e.g., in the case in which the dopant is electron acceptor (Shirakawa, 1983; Tanaka and Yamabe, 1983; Brédas, 1984).

1. In the dilute-doping regime the dopants extract the electrons from mobile solitons, which are neutral, leaving charged solitons (carbocations) (see Fig. 13a). Since the concentration of the neutral solitons is small, they are consumed almost immediately. Then, the electron transfer from the ordinary portion of the $(CH)_x$ chain takes place, yielding the cation radical (polaron) mentioned in Section II,D, as shown in the right-hand side of Fig. 13b.

2. As the concentration of the polarons increases (Fig. 13c), they become in close proximity, and two polarons recombine, leaving two charged solitons. This feature was first pointed out by Yamabe *et al.* (1981, 1982a) and has been examined by Brédas *et al.* (1982a). Charged solitons thus formed (Fig. 13d), being spinless, are responsible for the conduction in the lightly doped regime.

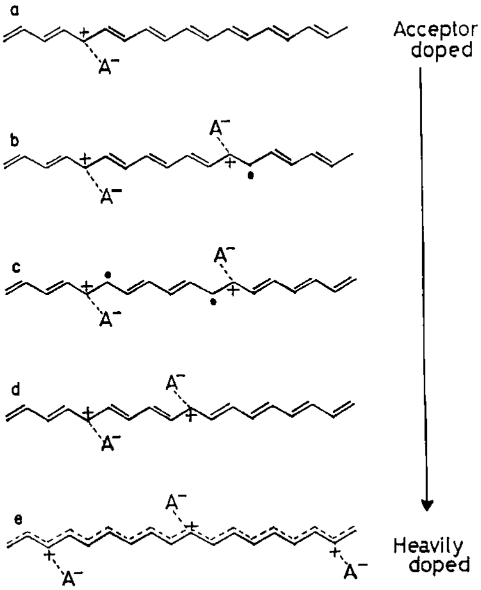


Fig. 13. Charged solitons and polarons in the *trans*-$(CH)_x$ due to various acceptor-doping levels (see text).

3. A heavy doping, with the concentration more than 7 mol%, results in the formation of one charged soliton per less than 14 carbon atoms, assuming a dopant molecule extracts an electron from the $(CH)_x$ chain. Hence the tails of adjacent charged solitons begin to overlap, signifying the disappearance of the bond alternations, as shown in Fig. 13e. In other words, a metallic state should occur through the "counter"-Peierls distortion. This tendency has been confirmed by the model calculations of the semiempirical one-dimensional tight-binding CO method with respect to a *trans*-$(CH)_x$ chain with one charged soliton per 11 to 5 carbon atoms (Yamabe *et al.*, 1984a). The extended Hückel calculation (Kertész *et al.*, 1982) has also predicted this feature in charge-transferred $(CH)_x$. Thus the reason why the Pauli susceptibility rapidly increases in this regime can be understood.

There has also been proposed a percolation transition based on the idea of the presence of metallic islands, apart from the soliton doping model (Tomkiewicz *et al.*, 1979, 1981).

Since a $(CH)_x$ chain consists of approximately 500 carbon atoms (Shirakawa *et al.*, 1980), it is also crucial to discuss the interchain conduction mechanism, which is indispensable for detecting actual electric conduction as a macroscopic phenomenon. Not many studies, however, have been done on this subject, except the work of Kivelson (1981, 1982). The concept of Kivelson's mechanism is based on the phonon-assisted intersoliton hopping of a neutral and a charged soliton between two chains, and, hence, applies to the case of the dilute limit of the dopant concentration.

It will be an interesting problem to analyze the intersoliton hopping mechanism assisted by a motion of the dopant molecule. We try to formulate here such an electron hopping process between two $(CH)_x$ chains (Yamabe *et al.*, 1984b), as illustrated in Fig. 14.

Let us consider a model system in which an electron transfers between two $(CH)_x$ chains at their centers of charged solitons: A and B separated by the distance $2R$. The total Hamiltonian of the system is designated by H_0, eigenfunctions and eigenvalues of which are ϕ_n and ε_n, respectively. Denoting the states in which the electron is localized at A and B by χ_A and χ_B, respectively, the two states ϕ_1 and ϕ_2 might be approximated by the linear combinations of χ_A and χ_B,

$$\begin{aligned}\phi_1 &= \frac{1}{\sqrt{2+2s}}(\chi_A + \chi_B)\\ \phi_2 &= \frac{1}{\sqrt{2-2s}}(\chi_A - \chi_B) \qquad (\varepsilon_2 > \varepsilon_1)\end{aligned} \tag{4}$$

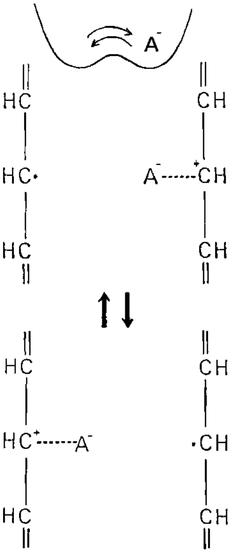


Fig. 14. Schematic representation of the proposed interchain conduction mechanism. Top is the energy potential for the motion of the dopant A$^-$.

where s is the overlap integral between χ_A and χ_B and is almost zero in the present case. The time required for the exchange of the electron, τ, is estimated by

$$\tau \sim h/2(\varepsilon_2 - \varepsilon_1) \tag{5}$$

which is very large, since the distance $2R$ is large ($2R = 7 \sim 8$ Å).

If this process, however, is assisted by a vibrational motion (with its frequency ν) of a dopant molecule charged by q, represented by

$$Z = D \cos(2\pi\nu t + \delta) \qquad 2D < 2R \tag{6}$$

where the Z axis is taken to be perpendicular to the chain direction and δ is the initial phase, it can be shown as follows that τ becomes much smaller. The vibrational motion of the dopant creates the perturbation H' as

$$H' = qh_e + qh_A + qh_B \tag{7}$$

where h_e is the Coulomb interaction between the charge of the dopant and the electron transferred, and h_A (h_B) is the Coulomb interaction between the charge of the dopant and the A (B) system. The interactions other than the long-range Coulomb term are neglected here and h_e, h_A, and h_B are explicitly time dependent. It is to be noted that the value of q can be adjusted so as to represent the screening effect between the dopant and the radical electron.

Thus the problem is to solve the following time-dependent Schrödinger equation.

$$\begin{aligned} &H = H_0 + H' \\ &i\frac{\partial}{\partial t}\Psi(t) = H\Psi(t) \qquad (\hbar = 1) \end{aligned} \tag{8}$$

Expanding $\Psi(t)$ by ϕ_n,

$$\Psi(t) = \sum_n C_n(t)\phi_n \exp(-i\varepsilon_n t) \tag{9}$$

the Schrödinger equation in Eq. (8) becomes a set of simultaneous equations.

$$\frac{dC_m(t)}{dt} = -i\sum_n C_n(t)H'_{mn} \exp(-2\pi i\nu_{mn}t) \tag{10}$$

$$\nu_{mn} = (\varepsilon_n - \varepsilon_m)/h$$

$$H'_{mn} = \int \phi_m^* H'\phi_n \, d\mathbf{r}$$

If we confine ourselves only to the transition between ϕ_1 and ϕ_2, Eq. (10) is reduced to

$$\begin{aligned} dC_1(t)/dt &= -iC_1(t)H'_{11} - iC_2(t)\exp(-2\pi i\nu_{12}t)H'_{12} \\ dC_2(t)/dt &= -iC_1(t)\exp(-2\pi i\nu_{12}t)H'_{21} - iC_2(t)H'_{22} \end{aligned} \tag{11}$$

In the first-order approximation, $C_1(t)$ and $C_2(t)$ are given by

$$\begin{aligned} C_1(t) &= \frac{1}{\sqrt{2}} - \frac{i}{\sqrt{2}}\int_0^t H'_{11}\,dt - \frac{i}{\sqrt{2}}\int_0^t \exp(-2\pi i\nu_{12}t)H'_{12}\,dt \\ C_2(t) &= \frac{1}{\sqrt{2}} - \frac{i}{\sqrt{2}}\int_0^t \exp(2\pi i\nu_{12}t)H'_{21}\,dt - \frac{i}{\sqrt{2}}\int_0^t H'_{22}\,dt \end{aligned} \tag{12}$$

where the electron is supposed to be localized at χ_A in the initial state. Denoting the time required for the exchange of the electron (assisted by the vibrational motion of the dopant) by τ', this quantity is given as the minimum positive value of t, which approximately satisfies

$$\{H'_{11}(t) + H'_{12}(t)\}^2 = 2\pi\nu_{12}H'_{12}(t) \tag{13}$$

after some straightforward algebra. Since the dopant molecule is assumed to move sinusoidally with the frequency ν, one can estimate that τ' is of the order of $1/\nu$ from Eq. (13). Therefore, it becomes clear that the electron hopping occurs as frequently as does the motion of the dopant.

III. Other Conjugated Systems

Conjugated polymers other than polyacetylene are also being actively investigated at present with respect to their practical use as conductive or semiconductive material. This kind of study has been particularly motivated due to the susceptibility of polyacetylene to undergo oxidation. One of the most promising groups of conjugated systems consists of polymers having condensed or connected aromatic rings. Although some polymers of this group have already been prepared (see, e.g., Baughman *et al.*, 1981, 1982), those with condensed aromatic rings have never been successfully synthesized, but quantum-chemical analysis of these polymers does provide information on effective polymer design for those who are engaged in the synthesis of conductive polymers in particular.

In this section we examine these polymers and discuss the electronic property that governs their physicochemical properties, particularly in relation to their electric behavior.

A. Conjugated Polymers with Condensed Aromatic Rings

Polymers belonging to this group lie in the area between $(CH)_x$ and graphite. For example, the H/C molar ratios of $(CH)_x$ and graphite are unity and zero, respectively, whereas polyacene, being a laddered polymer of two *trans*-$(CH)_x$ chains, has the H/C ratio 0.5. Some of the members of this group are illustrated in Fig. 15.

Polyacene is one of the simplest members of this group of polymers. Although it has not yet been successfully synthesized, there have been several studies on its electronic structure since the work of Salem and Longuet-Higgins (1960). Recent CNDO/2 calculation has claimed the most stable skeleton of polyacene to be as depicted in Fig. 15a (Tanaka *et al.*, 1983d). The band gap of polyacene is calculated to be 0.50 eV, which is surprisingly small for the Hartree–Fock type SCF-CO calculation. This is in contrast with the calculated band gap value, 10.64 eV, of polyphenanthrene (Fig. 15b), which is a geometrical isomer of polyacene. Polyphenanthrene is considered to be more "aromatic" than polyacene based on the discussion by Fukui (1976, 1982). Hence one can expect that polyacene will be a narrow-gap semiconductor with behavior similar to graphite.

This tendency is more enhanced in polyacenacene (Fig. 15c), which is considered to be a development of polyacene toward the direction of graphite. A preliminary estimation using the CNDO/2 method has shown

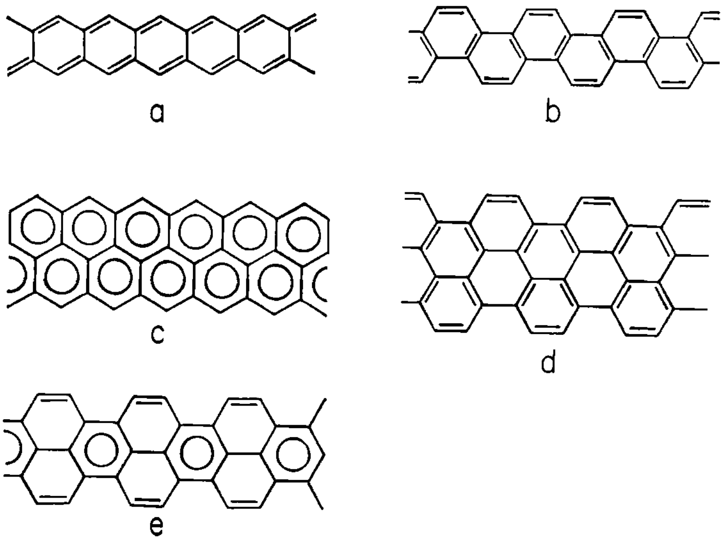


Fig. 15. Optimized skeletons of (a) polyacene, (b) polyphenanthrene, (c) polyacenacene, (d) polyphenanthrophenanthrene, and (e) polyperylene.

that the optimized skeleton of polyacenacene is of an equal C—C bond distance (Yamabe *et al.*, 1982e). The unit cell of this polymer consists of C_3H with an odd number of π electrons. Therefore, the HO and the LU bands stick together, signifying a metallic nature of this polymer as mentioned in the Section II,A. On the other hand, polyphenanthrophenanthrene (Fig. 15d), being a geometrical isomer of polyacenacene, has a band gap calculated to be 5.95 eV (Tanaka *et al.*, 1984d). Polyphenanthrophenanthrene is also considered to be a development of polyphenanthrene toward graphite.

All of these results show that the value of the band gap converges rapidly to zero with the growth of the skeleton toward the two-dimensional direction. Kertész and Hoffmann (1983) have examined the relationship of the decrease in the band gap in the framework of the Hückel Hamiltonian. By the same token, polyperylene, shown in Fig. 15e, is a graphitized version of poly(*p*-phenylene), which will be discussed in the next section, and has a smaller band gap, calculated to be 3.17 eV, than the 10.67-eV band gap calculated for poly(*p*-phenylene) (Tanaka *et al.*, 1984c). It would be of interest to note that all of these polymers have the HO and LU bands of π nature, the major coefficients of which consist in the carbon atoms on the perimeter of the polymer chain. Therefore, it is predicted that these polymers will be electrically conductive per se or under the introduction of adequate dopant, where the conduction carriers also secure their path on the perimeter of the chain.

Experimental attempts to synthesize any of the polymers described above have not been successful except a preliminary preparation of polyperylene (Murakami and Yoshimura, 1984). Alternative efforts are currently being made to obtain polyacenic material through pyrolysis of various organic polymers such as phenol-formaldehyde resin (Yamabe *et al.*, 1983; Tanaka *et al.*, 1984b), polyacrylonitrile (Teoh *et al.*, 1982, 1983), and poly(*p*-phenylene-1,3,4-oxadiazole) (Murakami *et al.*, 1983). The group of these pyrolytic polymers behaves rather like amorphous semiconductors and is considered to be composed of fragments of polyacene to graphite, that is, a sort of coke, coal, and so on.

The narrow-gap property of polyacenic members may be useful in the design of organic superconductors as the spine alternative to polyacetylene once employed by Little (1964).

B. Conjugated Polymers with Connected Aromatic Rings

Polymers in this category are of interest in that they can be easily synthesized, being of very high stability. A couple of these polymers are illustrated in Fig. 16. Poly(*p*-phenylene) is prepared by the polymerization of benzene with $AlCl_3$ and $CuCl_2$ (Kovacic and Kyriakis, 1963; Kovacic and Oziomek, 1964), whereas polypyrrole and polythienylene are prepared by the electrochemical polymerization of each monomer with an appropriate electrolyte (Diaz *et al.*, 1979; Tourillon and Garnier, 1982). Polythienylene is also synthesized by the polycondensation of dihalothiophene (Yamamoto *et al.*, 1980).

In poly(*p*-phenylene) the adjacent phenyl rings are rotated by about 22° with respect to one another [as determined from the X-ray diffraction data on *p*-phenylene oligomers (Delugeard *et al.*, 1976; Baudour *et al.*,

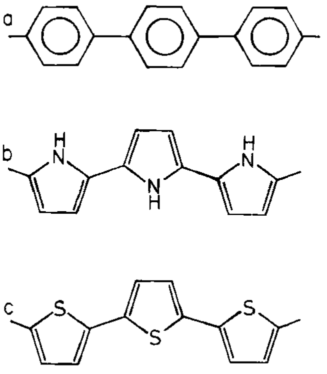


Fig. 16. (a) Poly(*p*-phenylene), (b) polypyrrole, and (c) polythienylene.

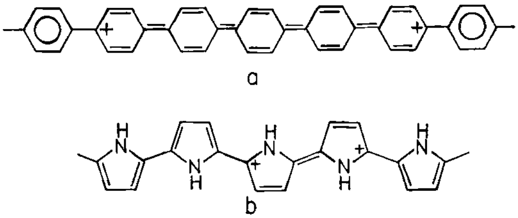


Fig. 17. Bipolarons in (a) poly(*p*-phenylene) and (b) polypyrrole.

1978)], which may be attributed to the repulsion between *o*-hydrogens of the adjacent rings. Poly(*p*-phenylene) shows a metallic conductivity of approximately 500 S cm^{-1} when it is doped, e.g., with AsF_5 (Shacklette *et al.*, 1979). Magnetic susceptibility measurement of the doped poly(*p*-phenylene) has shown only the existence of electric carriers that are spinless (Peo *et al.*, 1980). The contribution of bipolarons (a correlated charged-soliton/charged-antisoliton pair), seen in Fig. 17a, to the transport carrier, instead of charged solitons in $(CH)_x$, has therefore been examined by Brédas *et al.* (1982a). They have estimated that the extension of the bipolaron is over about five rings and that the formation of a bipolaron is favored by 0.4 eV more than the formation of two polarons. On the other hand, binding energy of a polaron (interaction energy between a charged defect and a neutral defect) has been estimated to be approximately 0.03 eV. The observed band gap of the pristine poly(*p*-phenylene) is 3.3 ~ 3.9 eV (Shacklette *et al.*, 1980; Watanabe *et al.*, 1981; Riga *et al.*, 1981). This quantity has also been estimated with the use of various effective Hamiltonians such as the extended Hückel (Whangbo *et al.*, 1979), the valence effective Hamiltonian (Brédas *et al.*, 1982b), and the CNDO/S3 (Ford *et al.*, 1983) methods. However, the actual poly(*p*-phenylene) chain involves 8 to 12 phenyl rings on an average (Froyer *et al.*, 1982), suggesting the oligomeric feature of this material. Therefore, in such a short chain length, the interchain conduction seems to be more crucial than for polyacetylene derivatives. We propose here a bipolaron hopping model, assisted by a simultaneous motion of two dopant molecules as illustrated in Fig. 18, as an interchain conduction mechanism. In this picture, two dopant molecules should be located not on opposing sides of the chain as shown in Fig. 19a, but on the same side as in Fig. 19b for the benefit of the simultaneous motion.

Polypyrrole and polythienylene (Fig. 16) have the same number of π electrons as poly(*p*-phenylene). The electronic structure of polypyrrole has been examined by several authors (Ford *et al.*, 1982; Brédas *et al.*, 1983a). The HO and the LU bands are of π nature. The orbital pattern of the HOMO accompanied by the top of the valence band has no contribu-

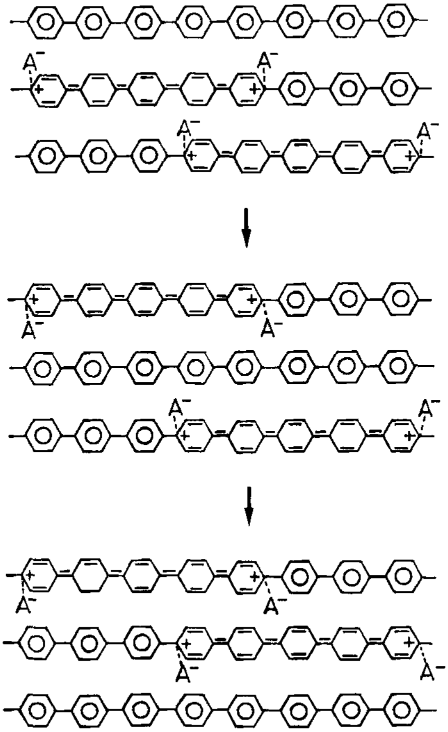


Fig. 18. Schematic representation of bipolaron hopping mechanism in poly(p-phenylene).

tion from nitrogen atoms due to symmetry of the polymer structure. This signifies that when polypyrrole is doped with the electron acceptor it attracts the π electrons not on the nitrogen atom but on the carbon skeleton. The same kind of feature has been noted with respect to polythienylene (Brédas *et al.*, 1983b; Tanaka *et al.*, 1983e). That is, the sulfur atom

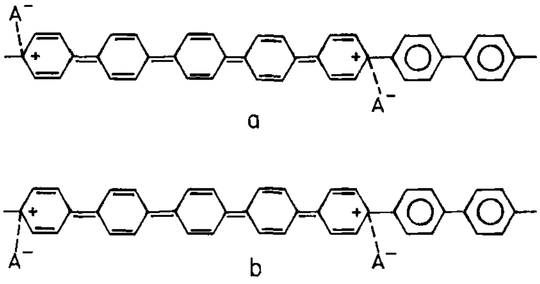


Fig. 19. Location of the dopant molecules A⁻ with respect to a poly(p-phenylene) chain.

has nothing to do with the electron acceptor. This tendency, as a matter of course, does not change if the sulfur atom is replaced with selenium or tellurium atoms. The ESR measurement of the doped and undoped polypyrrole has predicted that the transport carriers in this polymer are spinless (Scott *et al.*, 1983), and hence the possibility of the existence of a bipolaron as in Fig. 17b has been examined for the pyrrole oligomer (Brédas *et al.*, 1983c).

IV. Concluding Remarks

For the discussion of the physicochemical properties of conductive conjugated polymers, it is most important to set up the appropriate model and to employ the proper method of calculations. In this article most of the analyses have been based on the one-dimensional tight-binding CO methodology for polymers with periodical unit cells. This approach is useful because it gives not only the band structure but also information reflecting the nature of each atomic orbital in the unit cell.

Introduction of unperiodicity and randomness into the polymer system has also been provided in Section II,A. These features are particularly important in the discussion of the solid state properties of actual substance, and the methodology to deal with these ought to be established in the quantum-chemical area, certainly in cooperation with statistical mechanics.

The role of dopants should be clarified further. Although there have been some efforts to elucidate the electronic structure and spatial size of isolated dopants (Teramae *et al.*, 1982, 1983), almost no attempts have been made with respect to the treatment of the composite system of the polymer and the dopant except the work of Brédas *et al.* (1981). This is probably because of difficulty in the description of the electronic structure of the intermolecular charge-transfer complex with intermediate-range interactions using the current (ordinary) SCF-CO scheme. This will also be developed rapidly in the near future.

Finally, it is interesting to note that a fruitful concept such as solitons or polarons in conductive conjugated polymers has been introduced through quantum-chemical insight using the effective Hamiltonian of the Hückel level, not through "competition of the improvement of the basis set" using quantitative numerical calculations. Though admitting the importance of the quantitative calculations, this fact seems to suggest a fundamental attitude of quantum chemistry when it is concerned with interdisciplinary investigations.

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Some Aspects on the Hamiltonian and Liouvillian Formalism, the Special Propagator Methods, and the Equation of Motion Approach

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I. Introduction

In order to solve the Liouville equation in the general quantum theory of matter, the Liouvillian $\hat{L}$ defined through the relation $\hat{L}T \equiv HT - TH$

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and its resolvent $\hat{R} = (z \cdot 1 - \hat{L})^{-1}$ are considered as "superoperators" performing mappings of operators on operators. The Liouvillian eigenvalue problem $\hat{L}C = \nu C$ is investigated and its solution through the special propagator methods, the equation-of-motion approach, and their connection in terms of the commutator binary product are briefly reviewed. The solution of the eigenvalue problem $\hat{L}C = \nu C$ in the Hilbert–Schmidt operator space is then studied in greater detail. Starting from an arbitrary truncated basis **B** in the operator space, one may derive preliminary solutions, from which one then constructs refined solutions $D = |\Psi_f\rangle\langle\Psi_i|$ which automatically satisfy the algebraic conditions $D^2 = 0$, $D\hat{L}D = 0$, $DD^\dagger D = D$, etc. The refined solutions are expressed in terms of a new basis $\mathbf{B}^{(1)}$ which spans an operator space closed under adjunction (†) and multiplication. The refinement procedure is of particular value when separating an eigenelement associated with a degenerate eigenvalue ν into components which are excitation operators referring to specific initial and final states. The connection between the general theory and the special methods is then discussed using also the connection between the commutator binary product and the Hilbert–Schmidt binary product. In conclusion, the possibilities for further generalization of the propagator concept as well as approximations by means of "inner projections" are briefly discussed.

A. The Liouville Equation

In pure quantum mechanics, the fundamental problem is to determine the wave function $\Psi = \Psi(t)$, which satisfies the Schrödinger equation

$$-\frac{h}{2\pi i}\frac{\partial \Psi}{\partial t} = H\Psi, \tag{1.1}$$

from the initial condition $\Psi = \Psi_0$ for $t = t_0$. Here H is the Hamiltonian operator, which is usually assumed to be essentially self-adjoint and bounded from below: $H^\dagger = H$, $H > \alpha \cdot 1$. In quantum statistics,[1] on the other hand, the main problem is to determine the system operator Γ (or density matrix ρ) which satisfies the Liouville equation

$$-\frac{h}{2\pi i}\frac{\partial \Gamma}{\partial t} = H\Gamma - \Gamma H \tag{1.2}$$

from the initial condition $\Gamma = \Gamma_0$ for $t = t_0$. The system operators which are characterized by the properties[2]

$$\Gamma^\dagger = \Gamma, \qquad \Gamma > 0, \qquad \mathrm{Tr}\,\Gamma = 1, \tag{1.3}$$

form a *convex set*, the limit points of which satisfy the additional condition $\Gamma^2 = \Gamma$. In von Neumann's ensemble theory,[1] a system operator Γ

represents in general a "mixture"—except for the limit points which represent "homogeneous ensembles" and correspond to the case of pure quantum mechanics. In the latter case, the system opertor Γ is a primitive projector, the range of which is a one-dimensional linear manifold or "ray" $\Psi\alpha$; i.e., Γ defines a "wave function" Ψ. Conversely, one has the relation:

$$\Gamma = |\Psi\rangle\langle\Psi|\Psi\rangle^{-1}\langle\Psi|, \tag{1.4}$$

in terms of Dirac's brackets and ket–bra operators[3]; for some elementary rules as to the treatment of ket–bra operators, the reader is referred to Appendix A. In physics and chemistry, pure quantum mechanics is exactly valid only at the absolute zero of temperature ($T = 0$ K); it is also approximately applicable for systems where the ground state is situated far below the lowest excited state. However, in all other cases, one should really apply the more general rules of quantum statistics. For a system in thermal equilibrium at the temperature T, for instance, the system operator has the form

$$\Gamma = e^{(F-H)/kT} = Z^{-1}e^{-H/kT}, \tag{1.5}$$

corresponding to a "canonical ensemble"; the quantity $F = -kT \log Z$, called the "free energy," is determined by the normalization condition $\operatorname{Tr} \Gamma = 1$, which gives $Z = \operatorname{Tr} e^{-H/kT}$ for the so-called partition function Z. Systems which are not in thermal equilibrium have much more complicated system operators, of course, and this applies particularly to biological systems which may have a "temperature" but still are very far from equilibrium. It seems evident that, if the laws of physics are valid for the phenomena in molecular and submolecular biology involving the transfer of electrons, protons, atoms, and molecules, it has to be the general laws of "quantum statistics," and the solution of the Liouville equation (1.1) is hence also of fundamental importance in studying these types of phenomena.

B. The Liouvillian as a Superoperator

The operators T in ordinary quantum mechanics are defined as "mappings" of the elements Ψ in the wave function space $\{\Psi\}$ which serves as a "carrier space" for the operators. Similarly, one may consider mappings $\hat{M}$ of operators on operators, and they have obviously the operator space $\{T\}$ as their carrier space. One of the most fundamental superoperators is the *Liouvillian* $\hat{L}$, which is defined through the relation

$$\hat{L}T \equiv HT - TH, \tag{1.6}$$

where H is the Hamiltonian. Using this superoperator, one may now write the Liouville equation (1.2) in the form

$$-\frac{h}{2\pi i}\frac{\partial\Gamma}{\partial t} = \hat{L}\Gamma, \tag{1.7}$$

which is analogous to the time-dependent Schrödinger equation. The general idea is then to try to solve the Liouville equation by using the methods previously developed to solve the Schrödinger equation. For instance, if $S = S(t, t_0)$ is the Hamiltonian evolution operator satisfying the Schrödinger equation,

$$-\frac{h}{2\pi i}\frac{\partial S}{\partial t} = HS, \tag{1.8}$$

with the initial condition $S(t_0, t_0) = 1$ (= the identity operator), then one has the solution $\Psi(t) = S\Psi_0$. Similarly, if $\hat{S} = \hat{S}(t, t_0)$ is the *super-evolution-operator* satisfying the Liouville equation (1.7),

$$-\frac{h}{2\pi i}\frac{\partial\hat{S}}{\partial t} = \hat{L}\hat{S}, \tag{1.9}$$

with the initial condition $\hat{S}(t_0, t_0) = \hat{1}$ (= the identity superoperator), then one has the solution $\Gamma(t) = \hat{S}\Gamma_0$. Using (1.2) and (1.8) and the relation $SS^{-1} = 1$, it is easily shown that the Liouville equation has the explicit solution

$$\Gamma(t) = S\Gamma_0 S^{-1}, \tag{1.10}$$

and one may hence also define the super-evolution-operator $\hat{S}$ as a superoperator having the general property:

$$\hat{S}T \equiv STS^{-1}. \tag{1.11}$$

In the special case, when the Hamiltonian H is independent of time, one has the well-known explicit formula

$$S = e^{-\frac{2\pi i}{h}H(t-t_0)}, \tag{1.12}$$

and its counterpart in the superoperator space:

$$\hat{S} = e^{-\frac{2\pi i}{h}\hat{L}(t-t_0)}. \tag{1.13}$$

Even if these formulas in the beginning have a more symbolic meaning, they may be given a strict mathematical interpretation by properly defining the domains of the operators and superoperators involved. Usually the wave function space $\{\Psi\}$ is considered as a realization of the abstract Hilbert space based on a binary product $\langle\Psi_1|\Psi_2\rangle$ of the L^2-type:

$$\langle \Psi_1 | \Psi_2 \rangle = \int \Psi_1^* \Psi_2 \, dX, \tag{1.14}$$

and the operators T are then defined as mappings of this space. Similarly one may introduce an operator space $\{T\}$ consisting of all operators T having a finite *Hilbert–Schmidt* (HS) norm:

$$\|T\| = [\mathrm{Tr}\, T^\dagger T]^{1/2}, \tag{1.15}$$

and with the binary product

$$\{T_1 | T_2\} = \mathrm{Tr}\, T_1^\dagger T_2. \tag{1.16}$$

Such an operator space $\{T\}$ is another realization of the abstract Hilbert space, and the superoperators $\hat{M}$ are then conveniently defined as mappings of this space. In a previous paper,[4] it has been shown that—by using this general approach—one may generalize most of the L^2 methods earlier developed to solve the Schrödinger equation to solve also the Liouville equation. The purpose of the present article is to give some additional aspects of this problem, and particularly to show the connection with some of the so-called *propagator methods*.

C. Eigenvalue Problem of the Liouvillian

One of the important problems in the study of mappings is the stability problem, i.e., to divide their domains into irreducible subspaces which are stable under the mappings.[5] The starting point for such an investigation is the *eigenvalue problem*, i.e., the search for one-dimensional stable subspaces, since it automatically leads also to the search for irreducible stable subspaces of higher order, if such exists for the mappings under consideration. It is well known that the Hamiltonian H as a self-adjoint operator has only one-dimensional stable subspaces, and we will later see that this is also true for the Liouvillian $\hat{L}$. For a general discussion of the spectrum of H, the reader is referred elsewhere.[6]

Let us start by considering the Hamiltonian eigenvalue problem

$$H\Psi_k = E_k \Psi_k, \tag{1.17}$$

where the eigenfunctions Ψ_k are assumed to be quadratically integrable and normalized so that $\langle \Psi_k | \Psi_k \rangle = 1$. For the sake of simplicity, we will here assume that the spectrum $\{E_k\}$ is entirely *discrete*, even if there are no difficulties including also the continuum—one simply replaces the sum over k by a Stieltjes integral, which sums over the discrete index and integrates over the continuum. In addition to the Hamiltonian H, it is further convenient to consider its resolvent:

$$R(z) = (z \cdot 1 - H)^{-1}, \tag{1.18}$$

where z is a complex variable. The resolvent is self-adjoint for real values of z, whereas, for complex values of z, one has

$$\{R(z)\} = (z^* \cdot 1 - H)^{-1} = R(z^*). \tag{1.19}$$

It follows directly from (1.17) and (1.18) that the operators H and R have the same eigenfunctions

$$R\Psi_k = a_k\Psi_k, \tag{1.20}$$

whereas the eigenvalues are connected through the relation

$$a_k \equiv (z - E_k)^{-1}. \tag{1.21}$$

Even if in physics and chemistry the Hamiltonian is bounded from below to ensure the existence of a ground state of the system under consideration, the Hamiltonian H as a whole is an *unbounded* operator. It should be observed, however, that for values of z outside the small circles $|z - E_k| = \rho$, the resolvent $R(z)$ is always a *bounded* operator, and it is hence much easier to handle than the Hamiltonian itself; in addition, it has also much richer and mathematically interesting properties which are of essential value in studying the physical and chemical features of the system under consideration.

Let us now consider the eigenvalue problem for the Liouvillian superoperator $\hat{L}$ in the form

$$\hat{L}C = \nu C, \tag{1.22}$$

where the eigenelement C is supposed to satisfy certain boundary conditions, e.g., to have a finite Hilbert–Schmidt norm (1.15). It is clear from the definition (1.6) that any eigenelement is undetermined with respect to left and right multiplicative factors, which may be functions of H. It is further evident that any ket–bra operator

$$C = |\Psi_f\rangle\langle\Psi_i| \tag{1.23}$$

is an eigenelement to $\hat{L}$ associated with the eigenvalue

$$\nu = E_f - E_i, \tag{1.24}$$

which corresponds to an "excitation energy" from the initial state Ψ_i to the final state Ψ_f; here the index i refers to "initial" and the index f to "final." If the wave functions Ψ_i and Ψ_f are normalized to unity, one gets for the square of the HS-norm of C, according to (1.15):

$$||C||^2 = \mathrm{Tr}\, C^\dagger C = \langle\Psi_f|\Psi_f\rangle\langle\Psi_i|\Psi_i\rangle = 1. \tag{1.25}$$

Considering the operator $C^\dagger = |\Psi_i\rangle\langle\Psi_f|$ in greater detail, one gets further

$$\hat{L}C^\dagger = -\nu C^\dagger, \tag{1.26}$$

which means that, to every eigenvalue ν, there is also an eigenvalue $-\nu$; the spectrum of $\hat{L}$ is hence symmetric around the point $\nu = 0$. We note further that the case when $i = f$ corresponds to the eigenvalue $\nu = 0$, which is hence infinitely degenerate, having the eigenelements $|\Psi_k\rangle\langle\Psi_k|$. These results imply that, even if the Hamiltonian H is bounded from below, the spectrum of the Liouvillian $\hat{L}$ is *unbounded in both directions,* which is an important difference to remember when applying L^2 methods to the Liouvillian. For a more general discussion of the spectrum of the Liouvillian, the reader is referred elsewhere.[7]

The eigenoperators C and $C^\dagger$ are apparently excitation and de-excitation operators and, if one introduces a Fock space as a carrier space for the operators, one may also include ionization phenomena—removing or adding particles to the system under consideration.

Since the Hamiltonian H is self-adjoint the wave functions for the initial and final states are orthogonal and noninteracting with respect to H, so that

$$\langle\Psi_i|\Psi_f\rangle = 0, \qquad \langle\Psi_i|H|\Psi_f\rangle = 0. \tag{1.27}$$

This implies that the eigenoperator C defined by (1.23) will automatically satisfy the following relations:

$$C^2 = 0; \qquad C\hat{L}C = 0; \qquad CC^\dagger C = C, \tag{1.28}$$

which in the following will be referred to as the *algebraic conditions* for an excitation operator. The last relation implies that the operators $C^\dagger C$ and $CC^\dagger$ are idempotents which project onto one-dimensional subspaces spanned by the elements Ψ_i and Ψ_f, respectively. We note further that, if Ψ is an arbitrary wave function, one has the two relations

$$\begin{aligned} C\Psi &= \Psi_f\langle\Psi_i|\Psi\rangle \sim \Psi_f, \\ C^\dagger\Psi &= \Psi_i\langle\Psi_f|\Psi\rangle \sim \Psi_i. \end{aligned} \tag{1.29}$$

It is usually claimed that relations of the type (1.28) and (1.29) are of little interest in the practical applications, since one seldom has access to the *exact* eigenfunctions Ψ_i and Ψ_f for the initial and final states, respectively.

This is certainly true, but—at the same time—it should be observed that, if in some way one has calculated *approximate* wave functions $\overline{\Psi}_i$ and $\overline{\Psi}_f$ for the initial and final states, then the ket–bra operator

$$D = |\overline{\Psi}_f\rangle\langle\overline{\Psi}_i| \tag{1.30}$$

is an approximate excitation operator. If, further, the approximate eigenfunctions are orthogonal and noninteracting with respect to H, so that

$$\langle\overline{\Psi}_i|\overline{\Psi}_f\rangle = 0, \qquad \langle\overline{\Psi}_i|H|\overline{\Psi}_f\rangle = 0, \tag{1.31}$$

which is always the case when they are derived from the same Hamiltonian secular equation, then the operator D satisfies automatically the algebraic conditions (1.28), i.e.,

$$D^2 = 0, \qquad D\hat{L}D = 0, \qquad DD^\dagger D = D. \tag{1.32}$$

If Ψ is an arbitrary wave function, one gets finally

$$D\Psi \sim \overline{\Psi}_f, \qquad D^\dagger\Psi \sim \overline{\Psi}_i. \tag{1.33}$$

It should be observed, however, that in the literature many authors prefer to solve the eigenvalue problem (1.22) for the Liouvillian $\hat{L}$ directly in the operator space without any reference to the Hamiltonian formalism, to wave functions or ket–bra operators, and—in such a case—the algebraic conditions (1.32) are not necessarily satisfied for the approximate excitation operators D derived, and the study of these or similar conditions may become a special and sometimes crucial problem in the "direct approach."

In concluding this subsection, it should be observed that, in the same way that the Hamiltonian H has a resolvent $R(z)$ defined by (1.18), the Liouvillian $\hat{L}$ has a *superresolvent* $\hat{R}(z)$ defined through the relation

$$\hat{R}(z) \equiv (z \cdot \hat{1} - \hat{L})^{-1}. \tag{1.34}$$

Using (1.22) and (1.33), one easily shows that $\hat{R}$ has the same eigenelements C as the Liouvillian $\hat{L}$, i.e.,

$$\hat{R}C = bC, \tag{1.35}$$

where $b \equiv (z - \nu)^{-1}$. Even in this case, one may show that, for values of z outside the circles $|z - \nu| = \rho$, the superoperator $\hat{R}$ is a *bounded* superoperator. The superoperator $\hat{R}(z)$ has much richer properties than the Liouvillian itself, and it is much more feasible to describe the physical and chemical properties of the system under consideration.

In this subsection, it has been assumed that the Hamiltonian H—and hence also the Liouvillian $\hat{L}$—does not contain the time t explicitly, and the evolution operators S and $\hat{S}$ are then given by the simple formulas (1.12) and (1.13), respectively. In such a case, it should be remembered that the resolvents $R(z)$ and $\hat{R}(z)$ are the *Fourier transforms* of the evolution operators S and $\hat{S}$, respectively, provided that one introduces integration contours in the complex plane which enclose all poles of the resolvents in a positive sense.

In quantum statistics, the *expectation value* $\langle F\rangle$ of an operator F corresponding to a physical observable is given by the simple formula[2]:

$$\langle F\rangle = \mathrm{Tr}\, F\Gamma(t) = \mathrm{Tr}\, F(\hat{S}\Gamma_0), \tag{1.36}$$

and the Fourier transform of this quantity contains naturally the superresolvent $\hat{R}(z)$. One has also the alternative formula

$$\begin{aligned}\langle F\rangle &= \mathrm{Tr}\, F\Gamma(t) = \mathrm{Tr}\, FS\Gamma_0 S^{-1} \\ &= \mathrm{Tr}\, (S^{-1}FS)\Gamma_0 = \mathrm{Tr}\, F_{\mathrm{H}}\Gamma_0,\end{aligned} \tag{1.37}$$

where $F_{\mathrm{H}} = S^{-1}FS = \hat{S}^{-1}F$ is the Heisenberg representation of the operator F. In the case when Γ_0 corresponds to a *stationary state*, one has $\Gamma(t) = \Gamma_0$, and the expectation value (1.32) is then constant in time and contains no information as to the frequency distribution, etc. In this special case, it may be more convenient to study double-time correlation functions:

$$\langle F_{\mathrm{H}}(t)G_{\mathrm{H}}(t')\rangle = \mathrm{Tr}\, F_{\mathrm{H}}(t)G_{\mathrm{H}}(t')\Gamma_0, \tag{1.38}$$

which have Fourier transforms containing again the superresolvent $\hat{R}(z) \equiv (z \cdot \hat{1} - \hat{L})^{-1}$.

Using the simple operator identity $(A - B)^{-1} \equiv A^{-1} + (A - B)^{-1}BA^{-1}$, one finds that the superresolvent satisfies the equation

$$\hat{R}(z) = z^{-1} \cdot \hat{1} + z^{-1}\hat{R}(z)\hat{L}, \tag{1.39}$$

which is sometimes referred to as a "propagator relation," since one may substitute the left-hand side into the second term of the right-hand side, etc., which leads to a sequence of formulas where the superresolvent $\hat{R}(z)$ propagates more and more to the right until one finally obtains the infinite Neumann series for $\hat{R}(z)$. In the literature, there are many approaches which are described as "propagator methods," but they all seem to have the common feature that they involve the evaluation of the superresolvent $\hat{R}(z)$ in one way or another. In physics, there are also several other interpretations of the word "propagator."

It should finally be observed that, in the literature, the kernels of the Hamiltonian resolvent $R(z)$ and the Liouvillian superresolvent $\hat{R}(z)$ are often referred to as "Green's functions," and this means that resolvent techniques are often referred to as Green-function methods. Some of these methods are now so well developed and powerful that they are applied to the very large biomolecules in connection with the problem of the mechanism of chemical carcinogenesis.[8]

D. Special Propagator Methods

The propagator methods originally developed in quantum-fields theory[9] were rather simple in principle, but they became extremely complicated when applied in practice to many-particle systems, e.g., to the very large or infinite systems in quantum statistics,[10] or to atomic nuclei. In order to apply the propagator concept to statistical physics, very special methods had hence to be developed.[11] Even in nuclear physics, special techniques were studied,[12] and it soon became evident that is was necessary to develop "special propagator methods" which contained such drastic simplifications that practical calculations became possible.[13] It was well known[14] that, if an operator F is of particle rank p, i.e., if it involves interaction terms containing maximum p particles, then the evaluation of the expectation value $\langle F\rangle = \mathrm{Tr}\, F\Gamma$ requires only the knowledge of the reduced density matrix $\Gamma^{(p)}$ of order p. It was observed[15] that the commutator of two operators is of a lower particle rank than the product itself, and that it hence may be convenient to use *double commutators* or commutators of even higher orders in the theory to achieve the simplifications necessary to solve the so-called equation of motion (EOM).

Direct methods for determining excitation operators, ionization operators, etc., were developed by using specific bases in the operator space itself. Starting from a basis of one-particle functions, one could construct basic wave functions for many-particle systems of bosons and fermions by means of symmetrized or antisymmetrized products of one-particle functions. Introducing the creation and annihilation operators of the method of "second quantization,"[16] one could then introduce a basis in the many-particle operator space consisting of products of such operators or combinations called particle–hole operators. In the random-phase approximation (RPA), one used only a very limited basis in the operator space, consisting essentially of one-particle excitation operators, but the results were in many cases surprisingly good when applied to nuclear spectroscopy.

The special propagator methods were introduced into quantum chemistry around 1965 by Linderberg and Öhrn,[17] and during the last two decades there has been a tremendous development in this field.[18] If A and B are two arbitrary operators expressed in terms of second quantization, a *propagator* $\langle\langle A; B\rangle\rangle_z$ in their approach is a function of the complex variable z which satisfies the expansion formula:

$$\langle\langle A; B\rangle\rangle_z = z^{-1}\langle\phi|[B, A^\dagger]_\pm|\phi\rangle + z^{-1}\langle\langle A; \hat{L}B\rangle\rangle. \tag{1.40}$$

Here ϕ is a normalized *reference wave function,* and $[B, A^\dagger]_\pm$ is a commutator, where the plus sign holds for boson operators and the minus sign for fermions operators. Substituting $\hat{L}B$ instead of B in the left-hand side, one gets an expression for the second term in the right-hand side, etc., and this procedure leads to an expansion of the original propagator into expectation values of commutators of higher and higher orders:

$$\begin{aligned}\langle\langle A;B\rangle\rangle_z = {} & z^{-1}\langle\phi|[B, A^\dagger]_\pm|\phi\rangle \\ & + z^{-2}\langle\phi|[\hat{L}B, A^\dagger]_\pm|\phi\rangle \\ & + z^{-3}\langle\phi|[LLB, A^\dagger]_\pm|\phi\rangle + \cdots\end{aligned} \tag{1.41}$$

In the so-called *electron propagators,* one studies simultaneously the ionization potentials and the electron affinities of the system, whereas, in the so-called *polarization propagators,* one studies directly the excitation or de-excitation energies. By means of certain "decoupling procedures," Linderberg and Öhrn could construct approximate schemes for the practical computational evaluation of these propagators.

A completely different approach in trying to calculate the eigenvalues of the Liouvillian is rendered by the *equation-of-motion method,* which was developed in nuclear physics[12,13] and later introduced into quantum chemistry by several research groups.[19] The basic idea is to try to solve the eigenvalue problem (1.22) by expanding the approximate eigenelement D in terms of a truncated basis $\mathbf{B} = \{B_r\}$ of order m in the operator space, so that

$$D = \sum_{r=1}^{m} B_r d_r = \mathbf{Bd}, \tag{1.42}$$

where the problem is to determine the coefficients d_r. For this purpose, one considers the operator

$$\Omega = (\hat{L} - \nu \cdot 1)D, \tag{1.43}$$

which is vanishing for the exact solution $D = C$, and introduces the *reference function* ϕ and the associated basis functions:

$$\phi_r = B_r\phi, \tag{1.44}$$

which, for the sake of simplicity, are assumed to be linearly independent. It is evident that the approximate eigenelement D may have certain optimal properties, if the matrix elements

$$\Omega_{rs} = \langle\phi_r|\Omega|\phi_s\rangle \tag{1.45}$$

would be vanishing for all values of $r, s = 1, 2, \ldots, m$. However, since the equations obtained in that way are fairly complicated to handle, one starts from the necessary condition,

$$\langle\phi_r|\Omega|\phi\rangle = \langle\phi|B_r^\dagger\Omega|\phi\rangle = 0, \tag{1.46}$$

and combines it with a second necessary condition,

$$\langle\phi|\Omega B_r^\dagger|\phi\rangle = 0, \tag{1.47}$$

into a single relation

$$\langle\phi|[B_r^\dagger, \Omega]_\pm|\phi\rangle = 0, \tag{1.48}$$

which contains a *double commutator* and hence may be easier to handle. Substituting the expansion (1.42) into (1.48), one obtains a system of linear equations

$$\sum_{s=1}^{m} \langle\phi|[B_r^\dagger, (\hat{L} - \nu \cdot \hat{1})B_s]_\pm|\phi\rangle\, d_s = 0, \tag{1.49}$$

which has a nontrivial solution if and only if

$$|\langle\phi|[B_r^\dagger, (\hat{L} - \nu \cdot \hat{1})B_s]_\pm|\phi\rangle| = 0; \tag{1.50}$$

this is the *double-commutator secular equation* for the approximate eigenvalues ν. For a detailed discussion of the solutions to the equations (1.49), we will refer elsewhere.[13]

Here we will proceed in a slighly different way. Multiplying the relation (1.44) by d_r^* and summing over r from 1 to m, one obtains an equation of the type:

$$\langle\phi|[D^\dagger, \Omega]_\pm|\phi\rangle = \langle\phi|[D^\dagger, (\hat{L} - \nu \cdot \hat{1})D]_\pm|\phi\rangle = 0, \tag{1.51}$$

or

$$\langle\phi|D^\dagger(\hat{L}D) \pm (\hat{L}D)D^\dagger|\phi\rangle = \nu\langle\phi|D^\dagger D \pm DD^\dagger|\phi\rangle. \tag{1.52}$$

This means that the double-commutator quotient

$$I_1 = \frac{\langle\phi|D^\dagger(\hat{L}D) \pm (\hat{L}D)D^\dagger|\phi\rangle}{\langle\phi|D^\dagger D \pm DD^\dagger|\phi\rangle} \tag{1.53}$$

will give the approximate eigenvalues ν obtained from the secular equation (1.50) associated with the approximate eigenelements D. The same formula will, of course, give the exact eigenvalues ν for the exact eigenelements $D = C$.

Since the numerator and denominator in (1.53) are quadratic expressions in the approximate eigenelement D, one could perhaps expect that one could apply a variation principle to the quantity I_1 and derive the relations (1.49) in this way. Unfortunately there are some complications, since the first-order variations are not always identically vanishing, and these problems will be discussed in greater detail in a following section.

In order to study the structure of the theory in greater detail, Goscinski and his co-workers[20] introduce a binary product $(X|Y)$ of two elements X and Y of the operator space through the definition:

$$(X|Y) \equiv \langle\phi|YX^\dagger \pm X^\dagger Y|\phi\rangle, \tag{1.54}$$

where the upper sign holds for bosons and the lower sign for fermions. This binary product is linear in the second position and it has Hermitean symmetry, i.e.,

$$\begin{aligned}(X|Y_1, \alpha_1 + Y_2, \alpha_2) &= (X|Y_1)\alpha_1 + (X|Y_2)\alpha_2,\\ (Y|X) &= (X|Y)^*,\end{aligned} \tag{1.55}$$

but it is *degenerate* in the sense that, if $(X|Y) = 0$ for all operators X, this does not necessarily imply that $Y = 0$. Since this binary product contains a commutator, we will in the following discussion refer to it as a *commutator binary product* (CBP). It is ingeniously constructed to fit the Linderberg–Öhrn propagator theory and, starting from (1.36), Goscinski *et al.*[20] could show that the propagator has the explicit form:

$$\langle\langle A; B\rangle\rangle_z = (A|\hat{R}(z)|B), \tag{1.56}$$

where $\hat{R}(z)$ is the superresolvent defined by (1.34). By using (1.39), one can immediately check that the expansion formula (1.40) is satisfied. In this way, Goscinski *et al.* focused the attention on the properties of the superresolvent in connection with the special propagator theory.

Let us now also consider the eigenvalue problem (1.22) of the Liouvillian $\hat{L}$. Forming the CBP with an arbitrary operator D, one obtains

$$(D|\hat{L}C) = \nu(D|C) \tag{1.57}$$

or

$$\nu = (D|\hat{L}C)/(D|C), \tag{1.58}$$

which formula is still an exact expression for the eigenvalue ν. Replacing C by the approximate eigenelement D, one obtains instead the approximate eigenvalue formula

$$I_1 = \frac{(D|\hat{L}D)}{(D|D)} = \frac{\langle\phi|(\hat{L}D)D^\dagger \pm D^\dagger(\hat{L}D)|\phi\rangle}{\langle\phi|(DD^\dagger \pm D^\dagger D|\phi\rangle}, \tag{1.59}$$

which is indeed identical to (1.53) except that the terms here occur in a different order. The CBP is hence tailored to fit also the *equation-of-motion* method.

In operator theory, it is well known[21] that, if A is a linear operator having an inverse A^{-1} and if $\mathbf{h} = \{h_1, h_2, \ldots, h_n\}$ is a set of n linearly independent elements of the carrier space, then A may be approximated by an operator

$$A' = |\mathbf{h}\rangle\langle\mathbf{h}|A^{-1}|\mathbf{h}\rangle\langle\mathbf{h}| = \sum_{k,l=1}^{n} |h_k\rangle d_{kl}\langle h_l|, \tag{1.60}$$

where the coefficients d_{kl} are the elements of the matrix $\mathbf{d} = \langle \mathbf{h}|A^{-1}|\mathbf{h}\rangle^{-1}$. The operator A' is often referred to as the *inner projection* of A with respect to the set $\mathbf{h}$, and it may be shown that A' converges toward A when $n \to \infty$, and the set $\mathbf{h}$ becomes complete.[22]

Goscinski *et al.* applied boldly this inner projection technique to the superoperator space in order to obtain an approximation $\hat{R}(z)$ to the superresolvent $\hat{R}(z)$ in terms of the CBP and the basis $\mathbf{B} = \{B_1, B_2, \ldots, B_m\}$ in the operator space according to the formula:

$$\hat{R}'(z) = |\mathbf{B})(\mathbf{B}|z \cdot \hat{1} - \hat{L}|\mathbf{B})^{-1}(\mathbf{B}|. \tag{1.61}$$

In this way they could not only replace the previous decoupling procedures used in connection with the expansions (1.40) and (1.41) by more consistent approximations, but they could also show that the poles of the superoperator $\hat{R}'(z)$ were given by the zero points of the determinant

$$|(\mathbf{B}|\nu \cdot \hat{1} - \hat{L}|\mathbf{B})| = 0, \tag{1.62}$$

i.e., $|(B_r|(\hat{L} - \nu \cdot \hat{1})|B_s)| = 0$, or

$$|\langle\phi|[(\hat{L} - \nu \cdot \hat{1})B_s]B_r^\dagger \pm B_r^\dagger[(\hat{L} - \nu \cdot \hat{1})B_s]|\phi\rangle = 0, \tag{1.63}$$

which relation is identical to the double-commutator secular equation (1.50) in the *equation-of-motion* method.

It is hence evident that the CBP clarifies the structure of the special propagator theory in an excellent way. However, there is still a specific problem connected with the fact that the Liouvillian $\hat{L}$ is usually not self-adjoint with respect to this binary product:

$$(X|\hat{L}Y) \neq (\hat{L}X|Y), \tag{1.64}$$

except for very special reference functions ϕ, and this means that one does not know beforehand that the quotient $(D|\hat{L}D)/(D|D)$ in expression (1.59) is real. It should also be observed that, since the CBP is degenerate, it may be very difficult (if not impossible) to construct a meaningful adjoint to a superoperator $\hat{M}$ in general; we will return to this problem in a later section.

In concluding this subsection, we will discuss the properties of the approximate excitation operator $D = \mathbf{Bd}$ defined by (1.42) and (1.49) in somewhat greater detail. It is evident that, unless the basis $\mathbf{B}$ satisfies some special conditions, one cannot expect that the operator D should automatically fulfill the so-called *algebraic conditions* (1.32). In the special propagator method or the EOM method, one may hence have to be satisfied to impose somewhat weaker conditions.

For this purpose, it is here convenient to introduce a normalized reference function $\phi = \phi_i$, which is an approximation to the eigenfunction Ψ_i

for the initial state. In such a case, the function $D\phi$ should be an approximation to the eigenfunction Ψ_f for the final state, whereas the function $D^\dagger\phi$ should be approximately zero. If the relation

$$D^\dagger\phi = 0 \tag{1.65}$$

is exactly fulfilled, all calculations in the special propagator theory will be essentially simplified. The relation (1.65) is referred to as the *annihilation condition* or "killer condition," and it replaces to some extent the algebraic condition $D^2 = 0$ or the equivalent $(D^\dagger)^2 = 0$ in (1.32) but has a considerably weaker form.

If this relation is valid, the expressions (1.53) and (1.59) for the approximate eigenvalue l_1 simplify to the form

$$l_2 \equiv \langle\phi|D^\dagger(\hat{L}D)|\phi\rangle/\langle\phi|D^\dagger D|\phi\rangle, \tag{1.66}$$

which is often simpler to handle and is easier to compare with some of the standard variational expressions to be discussed later.

In the random-phase approximation, which was originally developed as a linearized extension of the time-dependent Hartree–Fock scheme, one uses an operator basis **B**, which consists solely of one-particle excitation operators. It was well known that the method would give theoretical results which were in good or reasonable agreement with experimental experience, but—for many years—an essential question was whether there existed a ground-state *reference function* ϕ associated with this particular operator basis, for which the annihilation condition (1.65) would be exactly satisfied. An analysis of Linderberg and Öhrn[23] showed finally that the appropriate reference function must have the form of an antisymmetrized geminal power (AGP):

$$\phi = O_{AS}g(1, 2)g(3, 4) \cdot \cdot \cdot g(2n - 1, 2n), \tag{1.67}$$

where O_{AS} is the antisymmetric projection operator; this function is obviously of the same form as the Bardeen–Cooper–Schrieffer (BCS) functions in the theory of superconductivity. It is well known that the AGP functions contain the Hartree–Fock functions as a special case but also, that from the very beginning, they contain a great deal more of particle correlation. Further studies and generalizations have, in this context, been developed by Goscinski and his collaborators.[24]

It should finally be observed that both the special propagator method and the EOM technique are built on the idea that, by using commutators of second and higher orders, one may essentially simplify the calculations, so that they involve only the *low-order reduced density matrices* $\Gamma^{(p)}$ of the reference state, which are in principle obtainable by successive trace formation[8] from the kernel $\Gamma(X|X') = \phi(X)\phi^*(X')$ of the reference state operator $\Gamma = |\phi)(\phi|$. The theory has the difficulties that the expressions (1.53) and (1.59) are not truly variational and that one is not from the very beginning certain that these expressions give *real* approximations to the Liouvillian eigenvalues ν due to the existence of the relation (1.64).

The question is whether one can today formulate the entire Liouvillian formalism in a more straightforward way, which would remove these difficulties, without increasing the volume and complexity of the calculations in an almost forbidding way. In this situation, one should certainly take advantage of the tremendous increase in computer capacity during the last decade—and particularly during the last few years. The purpose of this article is to discuss some of these problems, emphasizing particularly some of the theoretical points.

II. The Eigenvalue Problem for the Liouvillian in the Hilbert–Schmidt Theory

A. Hilbert–Schmidt's Operator Space

The classical operator space, which has been thoroughly investigated in mathematics almost since the beginning of this century, is the Hilbert–Schmidt (HS) space $\{A\}$ consisting of all operators A for which the product $A^\dagger A$ is a trace-class operator. A review of the use of the HS space as a carrier space for the superoperators in quantum theory has recently been given.[25]

In the HS space, an operator A is said to have the operator norm $\|A\|$ defined through the relation (1.15) or

$$\|A\|^2 = \operatorname{Tr} A^\dagger A = \sum_{k,l=1}^{\infty} |A_{lk}|^2 < \infty, \tag{2.1}$$

where $A_{lk} = (\varphi_l|A|\varphi_k)$ is the matrix element of A with respect to any complete orthonormal set $\{\varphi_k\}$. The HS binary product of two HS operators A and B is then introduced through the relation (1.16) or

$$\{A|B\} = \operatorname{Tr} A^\dagger B = \sum_{k,l=1}^{\infty} A_{lk}^* B_{lk}, \tag{2.2}$$

where the double sum is always absolutely convergent. It is easily checked that this binary product satisfies the first four axioms required by the binary product in an abstract Hilbert space: it is linear in the second position (ax. 1 and 2), it has Hermitean symmetry (ax. 3), and it is positive $\{A|A\} \geq 0$ and nondegenerate, i.e., $\{A|A\} = 0$ if and only if $A = 0$ (ax. 4). It may further be shown that the set $\{A\}$ contains all its limit points in the norm (ax. 5), and that there exists an enumerable set $\{A_1, A_2, A_3, \ldots\}$ which is everywhere dense in $\{A\}$ (ax. 6). This implies that the HS space

$\{A\}$ is another realization of the *abstract Hilbert space* in the sense of von Neumann.[1]

If $\hat{M}$ is a superoperator defined on $\{A\}$, one may now introduce its adjoint superoperator $\hat{M}^{\ddagger}$ through the relation

$$\{A|\hat{M}B\} = \{\hat{M}^{\ddagger}A|B\}, \tag{2.3}$$

and, if $\hat{M}^{\ddagger} = \hat{M}$, the superoperator $\hat{M}$ is said to be self-adjoint. For the sake of brevity, we will here omit the discussion of the domains of these operators, since it follows the general guidelines developed in the theory of the abstract Hilbert space. For the Liouvillian, one obtains

$$\begin{aligned}\{A|\hat{L}B\} &= \mathrm{Tr}\, A^{\dagger}(\hat{L}B) = \mathrm{Tr}\, A^{\dagger}(HB - BH) = \mathrm{Tr}(A^{\dagger}HB - HA^{\dagger}B)\\ &= \mathrm{Tr}(A^{\dagger}H - HA^{\dagger})B = \mathrm{Tr}(HA - AH)^{\dagger}B = \{\hat{L}A|B\},\end{aligned} \tag{2.4}$$

which shows that the superoperator $\hat{L}$ is *self-adjoint* with respect to the HS binary product. Considering the eigenvalue relation (1.22), this result implies that the eigenvalues ν of the Liouvillian are *real,* and that the eigenoperators C_r and C_s associated with different eigenvalues ν_r and ν_s are automatically *orthogonal* with respect to the HS binary product. The proof follows from the fact that, starting from the relations

$$\hat{L}C_r = \nu_r C_r, \qquad \hat{L}C_s = \nu_s C_s, \tag{2.5}$$

and using (2.4), one obtains directly

$$\nu_r^*\{C_r|C_s\} = \{\hat{L}C_r|C_s\} = \{C_r|\hat{L}C_s\} = \nu_s\{C_r|C_s\}, \tag{2.6}$$

i.e.,

$$(\nu_r^* - \nu_s)\{C_r|C_s\} = 0, \tag{2.7}$$

which proves the theorem.

According to (1.22) and (1.26), the eigenvalues ν of the Liouvillian $\hat{L}$ are distributed symmetrically around the point $\nu = 0$, and this implies that, even if the Hamiltonian H in physics is bounded from below, $H > \alpha \cdot 1$, the Liouvillian $\hat{L}$ is as a rule *unbounded.* Except for this difference, practically all the Hilbert-space methods developed to solve the Hamiltonian eigenvalue problem in exact or approximate form may be applied also to the Liouvillian eigenvalue problem. In the time-dependent case, the L^2 methods developed to solve the Schrödinger equation are now also applicable to solve the Liouville equation (1.7).

B. Variation Principle

Since the Liouvillian $\hat{L}$ is not bounded, one may wonder whether the so-called variation principle is still valid. For this purpose, we will consider the expression:

$$I = \{D|\hat{L}|D\}/\{D|D\} = \nu + \{D|\hat{L} - \nu \cdot \hat{1}|D\}/\{D|D\}, \tag{2.8}$$

where D is an arbitrary *trial operator* in the HS space. Putting $D = C + \delta C$, and using the relation $(\hat{L} - \nu \cdot \hat{1})C = 0$ and the fact that the superoperator $(\hat{L} - \nu \cdot \hat{1})$ is self-adjoint, one obtains directly

$$I = \nu + \{\delta C|\hat{L} - \nu \cdot \hat{1}|\delta C\}/\{D|D\}. \tag{2.9}$$

Since the first-order variation in δC is vanishing, one has the variational principle

$$\delta I = 0, \tag{2.10}$$

which indicates that if the trial operator D is a first-order approximation to the eigenoperator C, the expectation value I is a second-order approximation to the eigenvalue ν. Conversely, it may be shown that, if $\delta I = 0$, for *all* variations δC around a specific operator C, then C is necessarily an eigenoperator to $\hat{L}$ associated with the eigenvalue $\nu = I$. The variation principle is hence generally valid.

One may utilize this fact to construct approximate solutions to the eigenvalue problem (1.22) for the Liouvillian. For this purpose, we will introduce a set $\mathbf{B} = \{B_1, B_2, \ldots, B_m\}$ of m linearly independent HS operators in our operator space, and we will then try to expand the approximate eigenoperator D in this truncated basis, so that

$$D = \sum_{r=1}^{m} B_r d_r = \mathbf{Bd}, \tag{2.11}$$

in analogy with (1.42). The expectation value (2.8) takes now the form

$$I = \frac{\mathbf{d}^\dagger\{\mathbf{B}|\hat{L}\mathbf{B}\}\mathbf{d}}{\mathbf{d}^\dagger\{\mathbf{B}|\mathbf{B}\}\mathbf{d}} = \frac{\mathbf{d}^\dagger\mathbf{L}\mathbf{d}}{\mathbf{d}^\dagger\mathbf{\Delta}\mathbf{d}}, \tag{2.12}$$

where $\mathbf{L} = \{\mathbf{B}|\hat{L}\mathbf{B}\} = \{\mathbf{B}|H\mathbf{B} - \mathbf{B}H\}$ is the *Liouvillian matrix* having the elements

$$L_{rs} = \{B_r|\hat{L}|B_s\} = \mathrm{Tr}\, B_r^\dagger(HB_s - B_sH) = \mathrm{Tr}(B_r^\dagger HB_s - B_sHB_r^\dagger), \tag{2.13}$$

and $\mathbf{\Delta} = \{\mathbf{B}|\mathbf{B}\}$ is the *metric matrix* having the elements

$$\Delta_{rs} = \{B_r|B_s\} = \mathrm{Tr}\, B_r^\dagger B_s. \tag{2.14}$$

Varying the elements of the column vector $\mathbf{d}$ in (2.12) and applying the variation principle (2.10), one obtains the standard system of linear equations

$$(\mathbf{L} - I \cdot \mathbf{\Delta})\mathbf{d} = \mathbf{0}, \tag{2.15}$$

which has a nontrivial solution $\mathbf{d} \neq \mathbf{0}$, if and only if the secular equation

$$|\mathbf{L} - l \cdot \boldsymbol{\Delta}| = 0 \tag{2.16}$$

is satisfied. Starting from its eigenvalues $\lambda = l_1, l_2, \ldots, l_m$, one may then derive the associated eigenvectors $\mathbf{d}_1, \mathbf{d}_2, \ldots, \mathbf{d}_m$ and the corresponding approximate eigenoperators $D_1, D_2, \ldots, D_m$.

We note that, even if we start here from the same truncated basis $\mathbf{B} = \{B_1, B_2, \ldots, B_m\}$ as in the EOM method, the results are not necessarily the same, since (2.16) is a *single-commutator secular equation* whereas (1.50) is a *double-commutator secular equation.* It should be observed, however, that the column vectors $\mathbf{d}$ obtained by solving (2.15) are *optimal* in the sense of the variation principle, whereas this is not necessarily true for the vectors obtained by solving (1.49). In the following analysis, we will discuss the connection between these two approaches in somewhat greater detail. Since the variation principle (2.10) would provide an optimal approximation, the essential question is whether the theoretical and computational resources available today would permit the proper evaluation of the *single-commutator matrix elements* defined by (2.13) for a real many-particle system; this remains to be seen.

In concluding this subsection, we observe that, even if the approximate eigenvector D has been derived in an optimal way, there is no guarantee whatsoever that it will satisfy the algebraic relations (1.32) which are characteristic for an excitation operator, unless the truncated basis $\mathbf{B}$ satisfies some special conditions. Considering the product character of the algebraic conditions (1.32), it seems already natural to assume that a *necessary condition* will be that the set $\mathbf{B}$ is closed under adjunction (†) as well as under multiplication, so that

$$B_r B_s = \sum_{t=1}^{m} B_t a_{t,rs}, \tag{2.17}$$

since otherwise the discussion of the algebraic relations would take us outside the basis under consideration. We will return to the treatment of this important problem at a somewhat later stage.

C. Variation Principle for an Approximate Ket–Bra Excitation Operator; Adaption of a Solution to the Algebraic Conditions

In this subsection, we will from the very beginning assume that the approximate eigenoperator D has the form of an excitation (or de-excitation) operator according to (1.30), or

$$D = |\overline{\Psi}_{\mathrm{f}}\rangle\langle\overline{\Psi}_{\mathrm{i}}|, \tag{2.18}$$

where $\overline{\Psi}_{\mathrm{i}}$ and $\overline{\Psi}_{\mathrm{f}}$ are approximate eigenfunctions of the Hamiltonian H for the initial and final states involved. Assuming that these functions are normalized, orthogonal, and noninteracting with respect to H according to (1.31), one knows that the algebraic conditions (1.32) are automatically satisfied, and (2.18) is hence a convenient starting point for a discussion of these problems.

In order to derive an optimal approximation for the eigenoperator D, we will now apply the variation principle (2.10). One gets directly

$$\{D|D\} = \mathrm{Tr}\, D^{\dagger}D = \|\bar{\Psi}_{\mathrm{i}}\|^2 \cdot \|\bar{\Psi}_{\mathrm{f}}\|^2 = 1, \tag{2.19}$$

and

$$\begin{aligned} \{D|\hat{L}D\} &= \mathrm{Tr}\, D^{\dagger}(HD - DH) = \mathrm{Tr}(D^{\dagger}HD - DHD^{\dagger}) \\ &= \mathrm{Tr}[|\bar{\Psi}_{\mathrm{i}}\rangle\langle\bar{\Psi}_{\mathrm{f}}|H|\bar{\Psi}_{\mathrm{f}}\rangle\langle\bar{\Psi}_{\mathrm{i}}| - |\bar{\Psi}_{\mathrm{f}}\rangle\langle\bar{\Psi}_{\mathrm{i}}|H|\bar{\Psi}_{\mathrm{i}}\rangle\langle\bar{\Psi}_{\mathrm{f}}|] \\ &= \langle\bar{\Psi}_{\mathrm{f}}|H|\bar{\Psi}_{\mathrm{f}}\rangle - \langle\bar{\Psi}_{\mathrm{i}}|H|\bar{\Psi}_{\mathrm{i}}\rangle. \end{aligned} \tag{2.20}$$

Hence, one obtains for the variational quantity (2.8):

$$I = \langle\bar{\Psi}_{\mathrm{f}}|H|\bar{\Psi}_{\mathrm{f}}\rangle - \langle\bar{\Psi}_{\mathrm{i}}|H|\bar{\Psi}_{\mathrm{i}}\rangle. \tag{2.21}$$

This result implies that the variation principle $\delta I = 0$ for the Liouvillian in the case of an excitation operator (2.18) is closely connected with the variation principle $\delta\langle H\rangle = 0$ for the Hamiltonian. In the right-hand side of (2.21), one may hence vary the two functions $\bar{\Psi}_{\mathrm{i}}$ and $\bar{\Psi}_{\mathrm{f}}$ independently of each other, as long as they remain normalized, orthogonal, and noninteracting according to (1.31).

At first sight, this result may seem rather uninteresting, since one of the purposes of the Liouvillian formalism is to try to solve the eigenvalue problem (1.22) directly in the operator space. On the other hand, it may be of some value if the approximate eigenoperator $D = \mathbf{B}\mathbf{d}$ obtained by solving (2.15) and (2.18) does not automatically satisfy the algebraic relations (1.32). In such a case, one may proceed by introducing an arbitrary normalized reference function ϕ associated with the reference operator

$$\Gamma = |\phi\rangle\langle\phi|, \tag{2.22}$$

which is chosen so that it is easy to handle theoretically and computationally. Considering the set of functions $\{B_r\phi\}$ for $r = 1, 2, \ldots, m$, we will assume that it contains exactly p linearly independent elements, where $p \leq m$. This implies that the operator sets $\mathbf{B}\Gamma$ and $\Gamma\mathbf{B}$ also contain exactly p linearly independent elements.

In analogy with (1.33), we will now introduce some first rough estimates of the initial and final wave functions through the relations:

$$\phi_{\mathrm{f}} = D\phi, \qquad \phi_{\mathrm{i}} = D^{\dagger}\phi. \tag{2.23}$$

These unnormalized functions are usually neither orthogonal nor noninteracting with respect to H, but it is now possible to find linear combinations of these two functions which are normalized and satisfy the two conditions (1.31). The simplest way to achieve this result is to solve the Hamiltonian eigenvalue problem of order $n = 2$ with the two functions (2.23) as a basis.

For this purpose, we will momentarily write the basis in the form $\mathbf{\Phi} = \{\phi_1, \phi_2\}$, where $\phi_k = D_k\phi$ with $D_1 = D$ and $D_2 = D^\dagger$. For the Hamiltonian and metric matrices of order 2×2, one obtains respectively:

$$\begin{aligned} H_{kl} &= \langle\phi_k|H|\phi_l\rangle = \langle\phi|D_k^\dagger H D_l|\phi\rangle, \\ \Delta_{kl} &= \langle\phi_k|\phi_l\rangle = \langle\phi|D_k^\dagger D_l|\phi\rangle. \end{aligned} \tag{2.24}$$

In order to obtain a pair of two new approximate eigenfunctions to the Hamiltonian in the form $\overline{\Psi} = \mathbf{\Phi c}$, one has to evaluate the coefficients by solving the equation system:

$$(\mathbf{H} - \overline{E} \cdot \mathbf{\Delta})\mathbf{c} = \mathbf{0} \tag{2.25}$$

with the secular equation $|\mathbf{H} - \overline{E} \cdot \mathbf{\Delta}| = 0$ of order $n = 2$. Once the matrix elements have been evaluated, this is a trivial mathematical problem, and one obtains easily the two new approximate eigenfunctions:

$$\overline{\Psi}_{\mathrm{i}} = \mathbf{\Phi c}_{\mathrm{i}}, \qquad \overline{\Psi}_{\mathrm{f}} = \mathbf{\Phi c}_{\mathrm{f}}, \tag{2.26}$$

which satisfy the relations (1.31). This implies that if we construct a new approximate eigenoperator $D^{(1)}$ to the Liouvillian by means of the formula

$$D^{(1)} = |\overline{\Psi}_{\mathrm{f}}\rangle\langle\overline{\Psi}_{\mathrm{i}}|, \tag{2.27}$$

this operator will automatically satisfy the algebraic conditions (1.32). The approximate eigenvalue $\nu^{(1)}$ is then given by the relation (2.21), i.e., one has

$$\nu^{(1)} = \overline{E}_{\mathrm{f}} - \overline{E}_{\mathrm{i}}. \tag{2.28}$$

Starting from an approximate eigenelement $D = \mathbf{Bd}$ expressed in terms of the truncated basis $\mathbf{B}$ in the operator space, it is hence always possible to derive a new eigenelement $D^{(1)}$ which automatically satisfies the algebraic conditions (1.32).

In principle, this adaption procedure is very simple, and, if the reference function ϕ is conveniently chosen it may not be too difficult to evaluate the matrix elements in (2.24), which is the essential computational problem, of course.

We will now study the character of the new solution defined by (2.27). Substituting (2.26) into (2.27), one obtains

$$D^{(1)} = |\overline{\Psi}_{\mathrm{f}}\rangle\langle\overline{\Psi}_{\mathrm{i}}| = \tilde{\mathbf{c}}_{\mathrm{f}}|\tilde{\mathbf{\Phi}}\rangle\langle\mathbf{\Phi}|\mathbf{c}_{\mathrm{i}}^*, \tag{2.29}$$

where $|\tilde{\mathbf{\Phi}}\rangle\langle\mathbf{\Phi}|$ is a quadratic matrix of order 2 with ket–bra operators as elements:

$$\begin{aligned}|\tilde{\mathbf{\Phi}}\rangle\langle\mathbf{\Phi}| &= \begin{pmatrix}|\phi_1\rangle\langle\phi_1|, & |\phi_1\rangle\langle\phi_2| \\ |\phi_2\rangle\langle\phi_1|, & |\phi_2\rangle\langle\phi_2|\end{pmatrix} \\ &= \begin{pmatrix}D\Gamma D^\dagger, & D\Gamma D \\ D^\dagger\Gamma D^\dagger, & D^\dagger\Gamma D\end{pmatrix} = \begin{pmatrix}\tilde{\mathbf{d}}\tilde{\mathbf{B}}\Gamma\tilde{\mathbf{B}}^\dagger\mathbf{d}^* & \tilde{\mathbf{d}}\tilde{\mathbf{B}}\Gamma\mathbf{B}\mathbf{d} \\ \mathbf{d}^\dagger\mathbf{B}^\dagger\Gamma\tilde{\mathbf{B}}^\dagger\mathbf{d}^*, & \mathbf{d}^\dagger\mathbf{B}^\dagger\Gamma\mathbf{B}\mathbf{d}\end{pmatrix},\end{aligned} \tag{2.30}$$

where we have used the fact that $D = \mathbf{Bd} = \tilde{\mathbf{d}}\tilde{\mathbf{B}}$ and $D^\dagger = \mathbf{d}^\dagger\mathbf{B}^\dagger = \tilde{\mathbf{B}}^\dagger\mathbf{d}^*$, and the symbol ~ indicates taking the transpose of a matrix or vector, i.e., interchanging its rows and columns. The result implies that the new eigenelement $D^{(1)}$ is no longer expressed in terms of the original basis but in terms of the elements occurring in the four quadratic matrices:

$$\begin{matrix}\tilde{\mathbf{B}}\Gamma\tilde{\mathbf{B}}^\dagger; & \tilde{\mathbf{B}}\Gamma\mathbf{B}; \\ \mathbf{B}^\dagger\Gamma\tilde{\mathbf{B}}^\dagger; & \mathbf{B}^\dagger\Gamma\mathbf{B};\end{matrix} \tag{2.31}$$

from which one may select a *new operator basis* $\mathbf{B}^{(1)}$, consisting of the linearly independent elements in the four matrices (2.31). For a discussion of the order of this basis, the reader is referred to Appendix B; we note, however, that—in general—there is no reason why the new basis $\mathbf{B}^{(1)}$ should have the same order as the original basis $\mathbf{B}$. Since the two bases may further be different in character, it is clear that it is now necessary to repeat the entire procedure in terms of the new basis $\mathbf{B}^{(1)}$ to obtain an optimal solution.

This repetition procedure can be avoided only if the original basis $\mathbf{B}$ satisfies certain very special conditions. First of all, we will assume that the space spanned by the basis $\mathbf{B}$ is closed under adjunction (†), i.e., that in addition to each B_r also the adjoint operator $B_r^\dagger$ belongs to the space. This is most easily achieved by introducing the rule that non-self-adjoint basis elements always occur in adjoint pairs. If this is the case, one has the convenient theorem that, if $D = \mathbf{Bd}$ is an approximate eigenelement associated with the approximate eigenvalue ν, then

$$D^\dagger = \mathbf{d}^\dagger\mathbf{B}^\dagger = \tilde{\mathbf{B}}^\dagger\mathbf{d}^*, \tag{2.32}$$

is another approximate eigenelement in the same basis associated with the eigenvalue $-\nu$. We note that $\tilde{\mathbf{B}}^\dagger$ contains the same elements as $\mathbf{B}$ except for the order, i.e., $\tilde{\mathbf{B}}^\dagger$ is simply a permutation of $\mathbf{B}$.

Second, we will assume that the basis $\mathbf{B}$ is *closed under multiplication* according to (2.17). Finally, we will assume that the reference operator Γ defined by (2.22) belongs to the linear space spanned by the basis $\mathbf{B}$, i.e., that this space contains at least one primitive projector $\Gamma = \mathbf{B}\gamma = \tilde{\gamma}\mathbf{B}$, which satisfies the three relations $\Gamma = \Gamma^\dagger$, $\Gamma^2 = \Gamma$, and $\operatorname{Tr}\Gamma = 1$. If all these three conditions are fulfilled, then it is evident that all the elements in the four matrices (2.31) are linear combinations of the elements in the original basis **B**. We will later show that there exist also low-order examples of bases in the operator space having these properties.

It should be observed, however, that one cannot in general expect that an arbitrarily chosen basis **B** in the operator space should satisfy these three conditions, and this applies particularly to the particle–hole operator bases commonly used in the special propagator methods or the EOM approach. In such a case, the new operator basis $\mathbf{B}^{(1)}$ defined by the linearly independent elements in the four matrices (2.31) may serve as a new starting basis. Due to the construction, the basis $\mathbf{B}^{(1)}$ is automatically closed under adjunction (†). It is also clear that the basis $\mathbf{B}^{(1)}$ is closed under multiplication due to the fact that one has the multiplication rule

$$\Gamma\mathbf{B}_1\tilde{\mathbf{B}}_2\Gamma = |\phi\rangle\langle\phi|\mathbf{B}_1\tilde{\mathbf{B}}_2|\phi\rangle\langle\phi| = \mathbf{a}\Gamma, \tag{2.33}$$

where $\mathbf{a} = \langle\phi|\mathbf{B}_1\tilde{\mathbf{B}}_2|\phi\rangle$ is a matrix of order $m \times m$ consisting of numbers; here $\mathbf{B}_1$ and $\mathbf{B}_2$ stand temporarily as notations for either $\mathbf{B}$ or $\tilde{\mathbf{B}}^\dagger$. Hence multiplication of the elements in (2.31) will only give rise to elements in the linear space spanned by the new basis $\mathbf{B}^{(1)}$.

If the reference operator Γ does not belong to the original space **B**, it may be convenient to introduce the normalized reference function:

$$\phi_1 = D^\dagger\phi/\langle\phi|DD^\dagger|\phi\rangle^{1/2}, \tag{2.34}$$

which is proportional to the function ϕ_l defined by the second relation (2.23). In such a case, the new reference operator takes the form

$$\Gamma_1 = |\phi_1\rangle\langle\phi_1| = \frac{D^\dagger\Gamma D}{\langle\phi|DD^\dagger|\phi\rangle} = \frac{\mathbf{d}^\dagger\mathbf{B}^\dagger\Gamma\mathbf{B}\mathbf{d}}{\langle\phi|DD^\dagger|\phi\rangle}, \tag{2.35}$$

i.e., Γ_1 belongs to the space spanned by the basis $\mathbf{B}^{(1)}$. This implies that the basis $\mathbf{B}^{(1)}$ combined with the use of the new reference operator Γ_1 satisfies all three conditions outlined above, which means that, if one repeats the adaption procedure leading to a new excitation operator $D^{(2)}$ defined analogously to (2.29), one obtains automatically

$$\mathbf{B}^{(2)} \equiv \mathbf{B}^{(1)}, \tag{2.36}$$

and there is no more change of the basis in the operator space. The coefficients in the refined eigenelement $\bar{D}^{(1)} = \mathbf{B}^{(1)}\mathbf{d}^{(1)}$ should be determined by the variation principle (2.10), and it is clear that a second application of this variation principle is not going to change the result, i.e., that $D^{(2)} \equiv \bar{D}^{(1)}$.

It should be observed that the construction (2.27) is important from one more point of view. If the Liouvillian eigenvalue ν is *degenerate,* then the approximate eigenelement $D = \mathbf{B}\mathbf{d}$ obtained by means of the variation principle (2.10) may be a mixture of many types of excitation operators. For instance, in the case of the simple one-dimensional harmonic oscillator with the energy eigenvalues $E_n = (n + \frac{1}{2})\nu_0$, each one of the Liouvillian eigenvalues $\nu = 0, \pm\nu_0, \pm 2\nu_0, \ldots$ is infinitely degenerate. In such a case, the adaption procedure based on (2.27) leads to the *selection* of a specific component $D^{(1)}$ of the eigenoperator, which corresponds to particular excitation i → f, and this component is then refined to the form $D^{(2)} \equiv \bar{D}^{(1)}$.

The question of the simultaneous treatment of a set of excitation operators $D_1, D_2, \ldots, D_m$ will be postponed to a later stage of our discussion.

D. Connection with the Special Theories

Let us now compare the quantities I_1 and I_2 defined by the relations (1.53) and (1.66) in the special theories with the variational expression I defined by (2.8). In the special theories, one introduces usually a normalized reference function ϕ which is an approximation to the wave function for the initial state, so that $\phi = \phi_i$; as previously we will use the notation $\Gamma = |\phi\rangle\langle\phi|$ for the operator for the reference state. Starting from a given basis $\mathbf{B}$ in the operator space, we will further assume that we have constructed an approximate eigenoperator $D = \mathbf{B}\mathbf{d}$ by properly solving the double-commutator equations (1.49) and (1.50). The approximate unnormalized wave function for the final state is then given by the relation:

$$\phi_f = D\phi. \tag{2.37}$$

Let us further assume that the reference function ϕ satisfies the annihilation condition (1.65), i.e., that

$$D^\dagger\phi = 0. \tag{2.38}$$

In such a case, the quantity I_1 goes over into the quantity I_2, which we will now write in the form:

$$\begin{aligned} I_2 &= \frac{\langle\phi|D^\dagger(\hat{L}D)|\phi\rangle}{\langle\phi|D^\dagger D|\phi\rangle} = \frac{\langle\phi|D^\dagger HD - D^\dagger DH|\phi\rangle}{\langle\phi|D^\dagger D|\phi\rangle} \\ &= \frac{\langle\phi_f|H|\phi_f\rangle}{\langle\phi_f|\phi_f\rangle} - \frac{\langle\phi_1|H|\phi\rangle}{\langle\phi_1|\phi\rangle}, \end{aligned} \tag{2.39}$$

where we have temporarily introduced the notation $\phi_1 = D^\dagger D\phi$. The first term in the last member of (2.39) is an expectation value and has variational properties, whereas the second term is a so-called transition value which lacks variational properties.

In order to proceed, we observe that the two functions ϕ and ϕ_f obtained in this way are usually not orthogonal and further that the annihilation condition (2.38) is seldom exactly satisfied. Starting out from the approximate eigenoperator $D = \mathbf{Bd}$, we will now introduce a refined normalized wave function for the final state through the relation

$$\phi_f' = \frac{(1 - \Gamma)D\phi}{\langle\phi|D^\dagger(1 - \Gamma)D|\phi\rangle}, \tag{2.40}$$

by means of the projector $(1 - \Gamma)$; we have here arranged so that ϕ_f' becomes automatically orthogonal to the reference function ϕ, because of the property $(1 - \Gamma)\phi = 0$. Let us then define a new excitation operator D_1 by means of the ket–bra formula:

$$D_1 = |\phi_f'\rangle\langle\phi| = \frac{(1 - \Gamma)D\Gamma}{\langle\phi|D^\dagger(1 - \Gamma)D|\phi\rangle}. \tag{2.41}$$

Since ϕ_f' and ϕ are orthogonal, the annihilation condition

$$D_1^\dagger\phi = 0 \tag{2.42}$$

will be automatically satisfied, and this means that the quantity I_1 will go over into I_2. In evaluating the quantity I_2, we observe that

$$\phi_1' = D_1^\dagger D_1\phi = \Gamma\phi = \phi, \tag{2.43}$$

and, using (2.39), one obtains:

$$I_2 = \langle\phi_f'|H|\phi_f'\rangle - \langle\phi|H|\phi\rangle. \tag{2.44}$$

Substituting the excitation operator D_1 into the variational expression I, one obtains according to (2.21) that

$$I = \langle\phi_f'|H|\phi_f'\rangle - \langle\phi|H|\phi\rangle, \tag{2.45}$$

i.e., the quantities I_2 and I have become identical. This means that whenever the excitation operator D_1 has the form $D_1 = |\phi_f'\rangle\langle\phi|$, where ϕ_f' and ϕ are orthogonal, the quantity I_1 defined by (1.53) in the special theory becomes identical to the variational expression I defined by (2.8) in the Hilbert–Schmidt theory.

We note that the excitation operator D_1 defined by (2.41) is expressed in terms of the linearly independent operators in the sets $\mathbf{B}\Gamma$ and $\Gamma\mathbf{B}\Gamma \sim \Gamma$, which form a new basis; we note that the set $\mathbf{B}\Gamma$ as before contains exactly p linearly independent elements. It is evident that the coefficients in this basis are no longer necessarily optimal, and we may hence again start out with the double-commutator relations (1.49) and (1.50), etc., constructing an iteration procedure which—under certain conditions—may lead to "self-consistent solutions" in the sense that the Hilbert–Schmidt norm of the difference between two successive approximations has a value smaller than a given value ϵ, i.e., $\|D^{(n+1)} - D^{(n)}\| < \epsilon$.

It should be observed that the excitation operator D_1 defined by (2.41) will automatically satisfy the first and the third of the algebraic conditions (1.32), whereas the second is usually not satisfied unless the functions ϕ and ϕ_f' are noninteracting with respect to the Hamiltonian H, which is seldom the case.

In order to discuss also this aspect of the problem, we will return to the original approximate solution $D = \mathbf{Bd}$. The two functions ϕ and $\phi_f = D\phi$ are usually neither orthogonal nor noninteracting with respect to H and, in such a case, one can use the adaption procedure developed in the preceding subsection. Using the functions ϕ and ϕ_f as a basis of order 2 for a Hamiltonian eigenvalue problem, one obtains

$$\mathbf{H} = \begin{pmatrix} \langle\phi|H|\phi\rangle, & \langle\phi|HD|\phi\rangle \\ \langle\phi|D^{\dagger}H|\phi\rangle, & \langle\phi|D^{\dagger}HD|\phi\rangle \end{pmatrix}, \tag{2.46}$$

and

$$\boldsymbol{\Delta} = \begin{pmatrix} 1 & \langle\phi|D|\phi\rangle \\ \langle\phi|D^{\dagger}|\phi\rangle, & \langle\phi|D^{\dagger}D|\phi\rangle \end{pmatrix}. \tag{2.47}$$

The matrix elements are essentially the same as those occurring in (1.53), except that the double-commutator character is now lost. This property is very essential as a simplification in evaluating the m^2 matrix elements in the matrices occurring in (1.49) and (1.50), but it is of less importance in evaluating the few elements occurring in (2.44) and (2.47). The efforts involved in solving this computational problem is the price one has to pay to reach a more refined approximation. Solving the secular problem in the conventional way, one obtains two new normalized solutions

$$\phi_i^{(1)}, \qquad \phi_f^{(1)}, \tag{2.48}$$

which are automatically orthogonal and noninteracting with respect to H. Using these solutions, one may then construct a new excitation operator

$$D^{(2)} = |\phi_f^{(1)}\rangle\langle\phi_i^{(1)}|, \tag{2.49}$$

which satisfies all three algebraic conditions (1.32). By using the same reasoning as in the discussion of the relation (2.29), it is then easily seen that $D^{(2)}$ is expressible in terms of the linearly independent elements in products of the type $\mathbf{B\Gamma}$, $\mathbf{\Gamma B \Gamma} \sim \Gamma$, $\tilde{\mathbf{B}}\mathbf{\Gamma}\tilde{\mathbf{B}}^{\dagger}$, . . . etc.; for a more detailed discussion, the reader is referred to Appendix B, particularly relation

(B.7). It is hence clear that the entire problem will be essentially simplified if the set **B** contains Γ and is closed under adjunction (†) and multiplication. If not, one has to proceed as in the previous subsection and construct a new basis $\mathbf{B}^{(1)}$ in the operator space for which the relation (2.36) is going to be valid.

It is interesting to observe that, even if the coefficients **d** in the original approximate eigenelement $D = \mathbf{Bd}$ are determined by solving the equations (1.49) and (1.50) involving *double commutators,* the refined solutions (2.40) and (2.49) lead to situations where

$$I_1 = I_2 = I. \tag{2.50}$$

There seems hence to be a closer connection between the special theories and the general Hilbert–Schmidt approach than one would be originally inclined to expect. These problems will be further discussed in a later subsection.

E. Solution of the Liouvillian Eigenvalue Problem in a Ket–Bra Operator Basis

In the previous discussion, it was assumed that we could start from any truncated basis $\mathbf{B} = \{B_1, B_2, \ldots, B_m\}$ consisting of m linearly independent elements in the operator space. In this subsection, we will instead use a very special operator basis constructed by means of ket–bra operators $|b\rangle\langle a|$; in general, such operators have turned out to be very useful tools in going from a carrier space with a binary product $\langle a|b\rangle$ to the associated operator space.

It is easily shown[4] that, if $\varphi = \{\varphi_k\}$ is an orthonormal (ON) basis in the carrier space, then the ket–bra operators

$$P_{kl} = |\varphi_l\rangle\langle\varphi_k| \tag{2.51}$$

or *fundamental units* form an orthonormal basis in the HS operator space. In fact, one has

$$\begin{aligned}\{P_{kl}|P_{mn}\} &= \mathrm{Tr}\, P_{kl}^{\dagger}P_{mn} = \mathrm{Tr}\, P_{lk}P_{mn} = \mathrm{Tr}\, |\varphi_k\rangle\langle\varphi_l|\varphi_n\rangle\langle\varphi_m| \\ &= \langle\varphi_m|\varphi_k\rangle\langle\varphi_l|\varphi_n\rangle = \delta_{mk}\delta_{ln}.\end{aligned} \tag{2.52}$$

If $\varphi = \{\varphi_k\}$ is a truncated basis of order n in the carrier space, then the corresponding basis $\mathbf{P} = \{P_{kl}\}$ in the operator space is of order $m = n^2$. It may further be shown[4] that, if $n \to \infty$ and the basis $\varphi = \{\varphi_k\}$ becomes complete in the carrier space, then the basis $\mathbf{P} = \{P_{kl}\}$ becomes *complete* in the HS operator space. It should perhaps be observed that this completeness theorem is somewhat different in nature from the completeness theorems for products of particle–hole operators which are proven to be valid for finite (and infinite) configurational spaces and which are of essential importance in the current special propagator theories.[26] We note also that, since the relations

$$P_{kl}^{\dagger} = P_{lk}, \; P_{kl}P_{mn} = \delta_{kn}P_{ml} \tag{2.53}$$

are valid, the truncated basis **B** or order $m = n^2$ is closed under adjunction (†) and multiplication. If the reference function ϕ is chosen as a linear combination of the functions φ_k, the reference operator $\Gamma = |\phi\rangle\langle\phi|$ is further a linear combination of the fundamental units P_{kl}, i.e., Γ will belong to the space spanned by **P**.

In the following analysis, it is convenient to denote the double indices for the fundamental units by single symbols, so that $(k, l) = r$ and $(m, n) = s$. In such a case, the ON relation (2.52) may be written in the condensed form

$$\{P_r|P_s\} = \delta_{rs}. \tag{2.54}$$

Because of the completeness of the basis $\mathbf{P} = \{P_r\}$, it is now possible to expand the eigenoperator C exactly in the form

$$C = \sum_{r=1}^{\infty} P_r a_r, \qquad a_r = \{P_r|C\}. \tag{2.55}$$

However, if the basis φ is truncated to n elements, the operator basis **P** is truncated to $m = n^2$ elements, and one obtains an approximate eigenoperator of the form

$$D = \sum_{r=1}^{m} P_r d_r, \qquad d_r = \{P_r|D\}, \tag{2.56}$$

in accordance with (2.11). The variation principle (2.10) gives then the linear equation system (2.15) for the optimal vector **d** with $\mathbf{\Delta} = \mathbf{1}$, i.e.,

$$\mathbf{L}\mathbf{d} = l\mathbf{d}, \tag{2.57}$$

and the associated secular equation (2.16) is then of order $m = n^2$. Here $\mathbf{L} = \{L_{rs}\}$ is the Liouvillian matrix of order $m \times m$ having the elements

$$\begin{aligned} L_{rs} &= \{P_r|\hat{L}|P_s\} = \mathrm{Tr}\, P_r^{\dagger}(HP_s - P_sH) = \mathrm{Tr}(P_r^{\dagger}HP_s - P_sHP_r^{\dagger}) \\ &= \mathrm{Tr}\{|\varphi_k\rangle\langle\varphi_l|H|\varphi_n\rangle\langle\varphi_m| - |\varphi_n\rangle\langle\varphi_m|H|\varphi_k\rangle\langle\varphi_l|\} \\ &= \delta_{mk}H_{ln} - \delta_{ln}H_{mk}. \end{aligned} \tag{2.58}$$

In the computational technique of today, one may be able to handle secular problems of order $n = 10^6$ in the carrier space, and, since this implies $m = 10^{12}$, it seems at first sight as if the Liouvillian eigenvalue problem would be practically impossible to approach along this line. This is probably the reason why the ket–bra basis never has become popular in the current propagator theories or in the EOM method.[13]

It should be emphasized, however, that the Liouvillian matrix **L** in the Hilbert–Schmidt approach is diagonalized as easily as the Hamiltonian matrix **H**, provided that one starts with the latter problem. For those who insist that they would prefer to solve the Liouvillian eigenvalue problem without any reference to the Hamiltonian—except for the definition (1.6)—this is, of course, a setback, but already the discussion above has shown that the ket–bra formalism offers certain advantages which should certainly not be neglected.

Starting out from the truncated ON set $\boldsymbol{\varphi} = \{\varphi_k\}$ of order n in the carrier space, one may expand the approximate eigenfunction $\bar{\Psi}$ to the Hamiltonian H in the form:

$$\bar{\Psi} = \sum_{k=1}^{n} \varphi_k c_k = \boldsymbol{\varphi}\mathbf{c}. \tag{2.59}$$

The variation principle $\delta\langle H\rangle = 0$ leads then, in the usual way, to a system of linear equations:

$$\mathbf{H}\mathbf{c} = \bar{E}\mathbf{c}, \tag{2.60}$$

where **H** is the Hamiltonian matrix of order $n \times n$ having the elements $H_{kl} = \langle\varphi_k|H|\varphi_l\rangle$.

The secular equation $|\mathbf{H} - \lambda \cdot \mathbf{1}| = 0$ determines the eigenvalues $\lambda = \bar{E}_1, \bar{E}_2, \ldots, \bar{E}_n$ and solution of (2.60) gives then the eigenvectors $\mathbf{c}_1, \mathbf{c}_2, \ldots, \mathbf{c}_n$, which are assumed to be properly normalized to unity, and the corresponding approximate eigenfunctions $\bar{\Psi}_1, \bar{\Psi}_2, \ldots, \bar{\Psi}_n$. It should be observed that these functions are not only mutually orthogonal:

$$\langle\bar{\Psi}_k|\bar{\Psi}_l\rangle = \delta_{kl}, \tag{2.61}$$

but also noninteracting with respect to the Hamiltonian, which gives

$$\bar{H}_{kl} = \langle\bar{\Psi}_k|H|\bar{\Psi}_l\rangle = \bar{E}_k\delta_{kl}. \tag{2.62}$$

This means that the transformed basis $\bar{\boldsymbol{\Psi}} = \boldsymbol{\varphi}\mathbf{C}$, where $\mathbf{C} = \{\mathbf{c}_1, \mathbf{c}_2, \ldots, \mathbf{c}_n\}$ is a unitary matrix of order $n \times n$, diagonalizes the Hamiltonian matrix **H**.

Let us now introduce the fundamental units $\bar{\mathbf{P}}$ associated with the transformed basis, defined through the relation

$$\bar{P}_r = \bar{P}_{kl} = |\bar{\Psi}_l\rangle\langle\bar{\Psi}_k|. \tag{2.63}$$

Using (2.58) and (2.62), one obtains

$$\begin{aligned}\bar{L}_{rs} &= \{\bar{P}_r|\hat{L}|\bar{P}_s\} \\ &= \delta_{mk}\bar{H}_{ln} - \delta_{ln}\bar{H}_{mk} \\ &= \delta_{mk}\bar{E}_l\delta_{ln} - \delta_{ln}\bar{E}_k\delta_{mk} \\ &= \delta_{rs}(\bar{E}_l - \bar{E}_k) = \bar{\nu}_r\delta_{rs},\end{aligned} \tag{2.64}$$

where

$$\bar{\nu}_r = \bar{E}_l - \bar{E}_k. \tag{2.65}$$

This means that the Liouvillian matrix $\mathbf{L}$ of order $m = n^2$ is *automatically diagonalized* in terms of the basis $\bar{\mathbf{P}}$. For the associated approximate eigenelements, one obtains

$$\begin{aligned}\bar{P}_{\mathrm{if}} &= |\bar{\Psi}_{\mathrm{f}}\rangle\langle\bar{\Psi}_{\mathrm{i}}| = |\boldsymbol{\varphi}\mathbf{c}_{\mathrm{f}}\rangle\langle\boldsymbol{\varphi}\mathbf{c}_{\mathrm{i}}| = |\boldsymbol{\varphi}\rangle\mathbf{c}_{\mathrm{f}}\mathbf{c}_{\mathrm{i}}^{\dagger}\langle\boldsymbol{\varphi}| = |\boldsymbol{\varphi}\rangle\mathbf{d}\langle\boldsymbol{\varphi}| \\ &= \sum_{k,l=1}^{n} |\varphi_l\rangle d_{lk}\langle\varphi_k| = \sum_{k,l=1}^{n} P_{kl}d_{lk} \\ &= \sum_{r=1}^{m} P_r(\bar{\mathbf{d}})_r,\end{aligned} \tag{2.66}$$

where

$$\mathbf{d} = \mathbf{c}_{\mathrm{f}}\mathbf{c}_{\mathrm{i}}^{\dagger}, \tag{2.67}$$

and $\bar{D} = \bar{P}_{\mathrm{if}}$ is the approximate excitation operator desired. This method of diagonalizing the Liouvillian matrix $\mathbf{L}$ has the extra advantage that, if the eigenvalue ν is degenerate, the associated eigenelements $\bar{D}$ come out directly in the product form (2.66) referring to specific initial and final states.

F. Construction of an Optimal Basis

In this subsection, we will briefly discuss how one may construct a basis $\boldsymbol{\varphi} = \{\varphi_k\}$ of order n in the carrier space which is adapted not only to the treatment of the *ground state* of the Hamiltonian H but also to the study of the *lowest excited states*. In molecular and solid-state theory, it is often natural and convenient to start out from a set of n linearly independent wave functions $\boldsymbol{\Phi} = \{\Phi_k\}$ which are built up from atomic functions (spin orbitals, geminals, etc.) involved and which are hence usually of a *nonorthogonal* nature due to the overlap of the atomic elements. From this set $\boldsymbol{\Phi}$, one may then construct an orthonormal set $\boldsymbol{\varphi} = \boldsymbol{\Phi}\mathbf{A}$ by means of successive, symmetric, or canonical orthonormalization.[27] For instance, using the symmetric procedure, one obtains

$$\boldsymbol{\varphi} = \boldsymbol{\Phi}\langle\boldsymbol{\Phi}|\boldsymbol{\Phi}\rangle^{-1/2}, \qquad \langle\boldsymbol{\varphi}|\boldsymbol{\varphi}\rangle = 1, \tag{2.68}$$

and the set $\boldsymbol{\varphi} = \{\varphi_k\}$ may then be used as a truncated basis of order n for the wave function space. The sets $\boldsymbol{\Phi}$ and $\boldsymbol{\varphi}$ span hence a subspace of order n, which is characterized by the projector

$$Q = |\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}| = |\boldsymbol{\Phi}\rangle\langle\boldsymbol{\Phi}|\boldsymbol{\Phi}\rangle^{-1}\langle\boldsymbol{\Phi}|, \tag{2.69}$$

satisfying the relations

$$Q^2 = Q; \qquad Q^\dagger = Q; \qquad \mathrm{Tr}\, Q = n. \tag{2.70}$$

It may be shown[5] that one may solve the eigenvalue problem for H *exactly* within the subspace of Q, if and only if the projector Q reduces H, so that

$$HQ = QH. \tag{2.71}$$

This is very seldom the case, of course, and—in this situation—one may instead try to minimize the Hilbert–Schmidt norm of the operator

$$\Omega \equiv HQ - QH \tag{2.72}$$

or the expression

$$\|\Omega\|^2 = \mathrm{Tr}(H^2Q - HQHQ). \tag{2.73}$$

However, since this quantity involves the matrix elements of H^2, it may be cumbersome to evaluate.

If one is interested only in the n lowest eigenvalues, it may hence be more convenient to use a different approach, which is based on the fact that the Hamiltonian H is bounded from below: $H > \alpha \cdot \mathbf{1}$. It follows then from the Hylleraas–Undheim separation theorem[28] that the quantity

$$\begin{aligned}\omega &= \mathrm{Tr}\, HQ = \mathrm{Tr}\langle\boldsymbol{\Phi}|\boldsymbol{\Phi}\rangle^{-1}\langle\boldsymbol{\Phi}|H|\boldsymbol{\Phi}\rangle \\ &= \sum_{k,l=1}^{n} d_{kl}\langle\Phi_l|H|\Phi_k\rangle = \sum_{k=1}^{n} \langle\varphi_k|H|\varphi_k\rangle,\end{aligned}$$

where $\mathbf{d} = \langle\boldsymbol{\Phi}|\boldsymbol{\Phi}\rangle^{-1}$, is an *upper bound* to the sum of the n lowest eigenvalues, and that it takes its true minimum only when the projector Q reduces H. This expression is invariant under linear transformations $\boldsymbol{\Phi}' = \boldsymbol{\Phi}\boldsymbol{\alpha}$ of the basic set $\boldsymbol{\Phi}$, and one may hence concentrate one's interest on the choice of basis, its proper localization, and the variation of nonlinear parameters, etc. This is certainly a problem, where a great deal of research remains to be done.

At this point of our discussion, it may be convenient to take up the problem how one would treat n excitation operators $D_1, D_2, \ldots, D_n$ constructed from a common basis $\mathbf{B}$ of order m in the operator space *simultaneously*. The excitation operators are given in the form

$$D_k = \mathbf{B}\mathbf{d}_k = \tilde{\mathbf{d}}_k\tilde{\mathbf{B}}. \tag{2.75}$$

Starting out from the same normalized reference function ϕ as before, one may now introduce the following functions in the wave function space:

$$\phi_k = D_k\phi = \tilde{\mathbf{d}}_k(\tilde{\mathbf{B}}\phi). \tag{2.76}$$

Here we will assume that the reference function ϕ has been chosen so that all the functions ϕ_k are *linearly independent* and form a truncated basis $\mathbf{\Phi} = \{\phi_k\}$ of order m in the carrier space. We will again study the Hamiltonian eigenvalue problem in terms of this basis. The Hamiltonian and metric matrices are given by the expressions (2.24) with the difference that they are now of order $m \times m$. The approximate eigenfunctions are now given by the relations

$$\bar{\Psi}_k = \mathbf{\Phi}\mathbf{c}_k = \tilde{\mathbf{c}}_k\tilde{\mathbf{\Phi}}, \tag{2.77}$$

where the eigenvectors $\mathbf{c}_k$ are determined by solving the linear equation systems (2.25) with the associated secular equation $|\mathbf{H} - E\mathbf{\Delta}| = 0$ of order m. The refined excitation (and de-excitation) operators are then defined through the relations:

$$D^{(1)}_{kl} = |\bar{\Psi}_l\rangle\langle\bar{\Psi}_k| = \tilde{\mathbf{c}}_l|\tilde{\mathbf{\Phi}}\rangle\langle\mathbf{\Phi}|\mathbf{c}^*_k, \tag{2.78}$$

and the associated eigenvalues are given by the differences $\nu = \bar{E}_l - \bar{E}_k$. Here $|\tilde{\mathbf{\Phi}}\rangle\langle\mathbf{\Phi}|$ is a ket–bra matrix of order $m \times m$ having the special form:

$$|\tilde{\mathbf{\Phi}}\rangle\langle\mathbf{\Phi}| = \tilde{\mathbf{D}}\tilde{\mathbf{B}}|\phi\rangle\langle\phi|(\tilde{\mathbf{D}}\tilde{\mathbf{B}})^\dagger = \tilde{\mathbf{D}}\tilde{\mathbf{B}}\Gamma\tilde{\mathbf{B}}^\dagger\tilde{\mathbf{D}}^\dagger, \tag{2.79}$$

where $\mathbf{D} = (\mathbf{d}_1, \mathbf{d}_2, \ldots, \mathbf{d}_m)$ is a quadratic matrix consisting of all the column vectors $\mathbf{d}_1, \mathbf{d}_2, \ldots, \mathbf{d}_m$. We note that the product $\tilde{\mathbf{B}}\Gamma\tilde{\mathbf{B}}^\dagger$ contains the same type of linearly independent elements as occur in the four matrices (2.31), which together form a new basis $B^{(1)}$, which is closed under adjunction (†) and multiplication. If finally a new reference function $\phi^{(1)}$ is introduced as a linear superposition of the elements $\{\phi_k\}$, one obtains

$$\phi^{(1)} = \sum_k \phi_k a_k = \boldsymbol{\phi}\mathbf{a} = \tilde{\mathbf{a}}\tilde{\boldsymbol{\phi}} = \tilde{\mathbf{a}}\tilde{\mathbf{D}}(\tilde{\mathbf{B}}\phi), \tag{2.80}$$

and also

$$\Gamma^{(1)} = |\phi^{(1)}\rangle\langle\phi^{(1)}| = \tilde{\mathbf{a}}\tilde{\mathbf{D}}\tilde{\mathbf{B}}|\phi\rangle\langle\phi|(\tilde{\mathbf{a}}\tilde{\mathbf{D}}\tilde{\mathbf{B}})^\dagger = (\tilde{\mathbf{a}}\tilde{\mathbf{D}})\tilde{\mathbf{B}}\Gamma\tilde{\mathbf{B}}^\dagger(\tilde{\mathbf{D}}^\dagger\mathbf{a}^*), \tag{2.81}$$

which means that $\Gamma^{(1)}$ belongs to the space spanned by the new basis $\mathbf{B}^{(1)}$. If the entire procedure is repeated, the construction of the new excitation operators $D^{(2)}_{kl}$ is apparently not going to lead to any further extension of the basis in the operator space, and one obtains $\mathbf{B}^{(2)} \equiv \mathbf{B}^{(1)}$.

The method used here is general enough to include also the case when there are p linearly independent functions in the set $\{\Phi_k\}$ defined by (2.76) with $p \leq m$, in which case the new basis is of order p^2.

In concluding this subsection, we note that a basis of the ket–bra type $\mathbf{P} = \{P_{kl}\}$ is always orthonormal according to (2.54), whereas this is usually not true for an arbitrary basis $\mathbf{B} = \{B_1, B_2, \ldots, B_m\}$ in the operator space. However, even such a general basis may be brought to orthonormal form by means of successive, symmetric, or canonical orthonormalization.[19] Using the symmetric procedure, one obtains, e.g.,

$$\mathbf{A} = \mathbf{B}\{\mathbf{B}|\mathbf{B}\}^{-1/2}, \qquad \{\mathbf{A}|\mathbf{A}\} = \mathbf{1}, \tag{2.82}$$

and this transformation may sometimes simplify the theory as well as the applications.

G. Connection between the Various Approaches

Let us now study the connection between the Liouvillian formalism developed in terms of the Hilbert–Schmidt space and the double-commutator propagator theories or the EOM method. The special theories are based on linear equations of the type (1.49), or

$$\sum_{s=1}^{m} (L_{rs} - \nu\Delta_{rs})\, d_s = 0, \tag{2.83}$$

where the double-commutator Liouvillian matrix $\mathbf{L} = \{L_{rs}\}$ and the metric matrix $\boldsymbol{\Delta} = \{\Delta_{rs}\}$ have the following elements, respectively:

$$\begin{aligned} L_{rs} &= \langle\phi|[B_r^\dagger; \hat{L}B_s]_\pm|\phi\rangle \\ &= \langle\phi|B_r^\dagger(HB_s - B_sH) \pm (HB_s - B_sH)B_r^\dagger|\phi\rangle; \end{aligned} \tag{2.84}$$

$$\Delta_{rs} = \langle\phi|[B_r^\dagger; B_s]_\pm|\phi\rangle = \langle\phi|B_r^\dagger B_s \pm B_s B_r^\dagger|\phi\rangle, \tag{2.85}$$

where the upper sign is used for bosons and the lower for fermions. It should be remembered that these linear combinations were obtained by properly adding or subtracting the two relations (1.46) and (1.47), and that the conditions given here are *necessary* but usually not sufficient conditions for obtaining optimal solutions $\mathbf{d} = \{d_s\}$.

It should be observed that it does not matter whether one describes the operator space in terms of particle–hole operators in the language of second quantization or in terms of ket–bra operators. Choosing the ket–bra basis $\mathbf{P} = \{P_{kl}\}$ constructed from the orthonormal set $\boldsymbol{\varphi} = \{\varphi_k\}$ in the carrier space as our basis $\mathbf{B}$, one obtains for $r = (k, l)$ and $s = (m, n)$:

$$B_r^\dagger = P_{kl}^\dagger = |\varphi_k\rangle\langle\varphi_l|, \qquad B_s = P_{mn} = |\varphi_n\rangle\langle\varphi_m|. \tag{2.86}$$

Substitution into (2.84) and (2.85) gives then

$$\begin{aligned} L_{rs} = {} & \langle\phi|\varphi_k\rangle H_{ln}\langle\varphi_m|\phi\rangle - \delta_{ln}\langle\phi|\varphi_k\rangle\langle\varphi_m|H|\phi\rangle \\ & \pm \delta_{mk}\langle\phi|H|\varphi_n\rangle\langle\varphi_l|\phi\rangle \mp \langle\phi|\varphi_n\rangle H_{mk}\langle\varphi_l|\phi\rangle, \end{aligned} \tag{2.87}$$

$$\Delta_{rs} = \delta_{ln}\langle\phi|\varphi_k\rangle\langle\varphi_m|\phi\rangle \pm \delta_{mk}\langle\phi|\varphi_n\rangle\langle\varphi_l|\phi\rangle, \tag{2.88}$$

where $H_{kl} = \langle\varphi_k|H|\varphi_l\rangle$ as usual. Let us assume that we have solved the Hamiltonian eigenvalue problem within the subspace spanned by the set $\boldsymbol{\varphi} = \{\varphi_k\}$, and that we have obtained the approximate eigenfunctions $\bar{\boldsymbol{\Psi}} = \boldsymbol{\varphi}\mathbf{C}$ which are orthogonal and noninteracting according to (2.61) and (2.62), respectively. Introducing the transformed basis $\bar{\mathbf{P}} = \{\bar{P}_{kl}\}$, where $\bar{P}_{kl} = |\bar{\Psi}_l\rangle\langle\bar{\Psi}_k|$, and using (2.62), one obtains

$$\begin{aligned}\bar{L}_{rs} = {} & \bar{E}_l\delta_{ln}\langle\phi|\bar{\Psi}_k\rangle\langle\bar{\Psi}_m|\phi\rangle - \delta_{ln}\langle\phi|\bar{\Psi}_k\rangle\langle\bar{\Psi}_m|H|\phi\rangle \\ & \pm \delta_{mk}\langle\phi|H|\bar{\Psi}_n\rangle\langle\bar{\Psi}_l|\phi\rangle \mp \bar{E}_m\delta_{mk}\langle\phi|\bar{\Psi}_n\rangle\langle\bar{\Psi}_l|\phi\rangle.\end{aligned} \tag{2.89}$$

For the diagonal elements, one has $r = s$, i.e., $k = l$ and $m = n$, and they are hence usually nonvanishing. For the *nondiagonal elements*, one has $r \neq s$, i.e., $k \neq m$ or $l \neq n$ or both, and since all terms in (2.89) and (2.87) contain the factor δ_{mk} or the factor δ_{ln}, one gets

$$L_{rs} = 0, \qquad \bar{\Delta}_{rs} = 0, \qquad r \neq s \tag{2.90}$$

This means that the approximate eigenbasis $\bar{\mathbf{P}}$ diagonalizes both the double-commutator Liouvillian matrix and the metric matrix for an arbitrary reference function ϕ.

If one chooses the reference function as one of the approximate eigenfunctions, so that $\phi = \bar{\Psi}_{\mathrm{i}}$, one obtains for the diagonal elements:

$$\bar{L}_{rr} = \delta_{\mathrm{i}k}(\bar{E}_l - \bar{E}_k) \pm \delta_{\mathrm{i}l}(\bar{E}_{\mathrm{i}} - \bar{E}_k), \tag{2.91}$$

$$\bar{\Delta}_{rr} = \delta_{\mathrm{i}k} \pm \delta_{\mathrm{i}l}. \tag{2.92}$$

These results indicate that the double-commutator Liouvillian matrix has rather different properties compared to the ordinary matrix (2.64), and that the eigenvalues in the form of energy differences have a different form. It should also be observed that the solutions to the linear equation system (2.83) may have a rather different character.[13]

In concluding this subsection, we note that the main purpose of the double-commutator approach is to provide a method, wherein one can evaluate the matrix element L_{rs} and Δ_{rs} in (2.83) with the theory and computational tools available and then determine the approximate eigenvalues ν without reference to the Hamiltonian formalism, i.e., without using the formula $\nu = \bar{E}_{\mathrm{f}} - \bar{E}_{\mathrm{i}}$, which contains the difference between two large numbers. In this connection, it may be of value to observe the validity of the relation (2.50) in the reverse order, i.e., $I = I_2 = I_1$, which implies that it is possible to evaluate the approximate eigenvalues I in the ordinary formalism based on (2.8) in terms of the quantity I_1 defined by (1.53) in the double-commutator formalism. It should also be observed that, if the original basis in the wave function space is built up from specific atomic elements, then it may be possible to arrange so that large common parts in the eigenvalues $\bar{E}_i$ and $\bar{E}_f$ cancel identically in forming the difference $\nu = \bar{E}_f - \bar{E}_i$, and to treat excitation energies in the same way as one may treat cohesive energies.[29]

In the next section, we will study the connection between the various methods in somewhat greater detail by using a different approach to the entire problem.

III. Connection between the Binary Products in the Operator Space

A. General Binary Products and the Concept of Adjoint Pairs of Superoperators

A superoperator $\hat{G}$ defined on the Hilbert–Schmidt operator space is said to be *bounded,* if it satisfies the inequality

$$||\hat{G}A|| \leq K(\hat{G}) \cdot ||A||, \tag{3.1}$$

where $K = K(\hat{G})$ is a positive number. Let us now consider the quantity

$$[A|B] = \{A|\hat{G}B\} = \operatorname{Tr} A^{\dagger}(\hat{G}B), \tag{3.2}$$

where the superoperator $\hat{G}$ has the additional properties

$$\hat{G}^{\dagger} = \hat{G}, \qquad \hat{G} > 0. \tag{3.3}$$

It is easily checked that the quantity $[A|B]$ satisfies the first four axioms of a binary product in the theory of the abstract Hilbert space, and, for this reason, the quantity $[A|B]$ will be referred to as a *general binary product,* and the bounded superoperator $\hat{G}$ as a *metric superoperator.* Conversely, one may also show that any binary product $[A|B]$, which satisfies the first four axioms, may be written in the form (3.2).

In the definition (2.3), the concept of a pair of adjoint superoperators—$\hat{M}$ and $\hat{M}^{\ddagger}$—is related to the HS binary product. Similarly, one may now introduce *a pair of adjoint superoperators—$\hat{M}$* and $\hat{N}$—through the general binary product

$$[A|\hat{M}B] = [\hat{N}A|B], \tag{3.4}$$

and the question is now how the two concepts are related. The metric operator $\hat{G}$ is positive definite, and we will now explicitly assume that it defines a one-to-one mapping of the operator space and has an inverse $\hat{G}^{-1}$. Using (3.4) and (3.2), one obtains

$$\begin{aligned}[\hat{N}A|B] &= [A|\hat{M}B] = \{A|\hat{G}\hat{M}B\} = \{\hat{M}^{\ddagger}\hat{G}A|B\} \\ &= \{\hat{G}^{-1}\hat{M}^{\ddagger}\hat{G}A|\hat{G}B\} = [(\hat{G}^{-1}\hat{M}^{\ddagger}\hat{G})A|B],\end{aligned} \tag{3.5}$$

and

$$\hat{N} = \hat{G}^{-1}\hat{M}^{\ddagger}\hat{G}. \tag{3.6}$$

The result implies that the adjoint $\hat{N}$ of $\hat{M}$ with respect to a general binary product is a *similarity transformation* of the adjoint $\hat{M}^{\ddagger}$ with respect to the HS binary product.

It follows that, if the superoperator $\hat{M}$ is "self-adjoint" with respect to any general binary product, it has always real eigenvalues, and its eigenoperators are orthogonal with respect to this binary product. In the definition (3.2), we have defined the general binary product in terms of the HS binary product, but it is evident that we could have used any binary product satisfying the first four axioms as a starting point or "reference binary product."

The HS binary product has the property that the Liouvillian superoperator $\hat{L}$ is *self-adjoint* according to (2.4) in this representation, and, for this reason, the HS binary product is the natural reference product in the Liouvillian formalism.

B. Bivariational Principle

It should be observed that, even if the superoperator $\hat{M}$ is not self-adjoint, the pair of adjoint superoperators—$\hat{M}$ and $\hat{N}$—may have rather interesting properties.[5] Let us assume that $\hat{M}$ and $\hat{N}$ have eigenvalue relations of the type:

$$\hat{M}A_k = m_k A_k, \qquad \hat{N}B_l = n_l B_l. \tag{3.7}$$

In such a case, one obtains

$$n_l^*[B_l|A_k] = [\hat{N}B_l|A_k] = [B_l|\hat{M}A_k] = m_k[B_l|A_k], \tag{3.8}$$

i.e.,

$$(n_l^* - M_k)[B_l|A_k] = 0. \tag{3.9}$$

If $n_l^* \neq m_k$, one gets

$$[B_l|A_k] = 0, \tag{3.10}$$

which is the so-called *biorthogonality theorem*. If $[B_k|A_k] \neq 0$, one obtains $n_k = m_k^*$, which means that the eigenvalues of $\hat{N}$ and $\hat{M}$ usually occur as conjugate complex numbers. Instead of (3.7), one can then write

$$(\hat{M} - m_k \cdot \hat{1})A_k = 0, \qquad (\hat{N} - m_k^* \cdot \hat{1})B_k = 0, \tag{3.11}$$

where $(\hat{N} - m_k^* \cdot \hat{1})$ and $(\hat{M} - m_k \cdot \hat{1})$ are adjoint superoperators. Let us now consider the bivariational expression:

$$I = \frac{[B|\hat{M}|A]}{[B|A]} = m + \frac{[B|\hat{M} - m \cdot \hat{1}|A]}{[B|A]}, \tag{3.12}$$

under the assumption that $[B|A] \neq 0$. Here we will let A and B be trial operators, which are variations of the exact eigenoperators A_k and B_k:

$$A = A_k + \delta A, \qquad B = B_k + \delta B. \tag{3.13}$$

Putting $m = m_k$ and using (3.4) and (3.11), one obtains

$$I = m_k + \frac{[\delta B|\hat{M} - m_k \cdot \hat{1}|\delta A]}{[B|A]}, \tag{3.14}$$

where the first-order variation is vanishing, so that

$$\delta I = 0. \tag{3.15}$$

This relation is sometimes referred to as the *bivariational principle*,[5] and it plays an important role in the current literature.

It should be observed that the brief treatment here is essentially oversimplified, since the eigenvalue problem (3.7) is not sufficient to characterize a general superoperator and has to be replaced by the so-called *stability problem*. This is also related to the fact that a general quadratic matrix cannot be brought to diagonal form by means of a similarity transformation—in fact, it can only be brought to the so-called *classical canonical form* consisting of Jordan blocks described by Segré characteristics. Even the bivariational principle has then to be generalized. For details, the reader is referred elsewhere.[5]

C. The Commutator Binary Product

The special binary product (1.54) introduced by Goscinski and coworkers[14] has played an important role in revealing the structure of current propagator theory, and we will now try to relate it to the HS binary product. Introducing the self-adjoint projector

$$\Gamma = |\phi\rangle\langle\phi|, \tag{3.16}$$

associated with the reference function ϕ, one obtains directly:

$$\begin{aligned}(X|Y) &\equiv \langle\phi|YX^\dagger \pm X^\dagger Y|\phi\rangle = \mathrm{Tr}(YX^\dagger\Gamma \pm X^\dagger Y\Gamma) \\ &= \mathrm{Tr}\, X^\dagger(\Gamma Y \pm Y\Gamma) = \{X|\Gamma Y \pm Y\Gamma\}.\end{aligned} \tag{3.17}$$

Introducing the reference superoperator $\hat{\Gamma}$ through the definition

$$\hat{\Gamma}T \equiv \Gamma T \pm T\Gamma, \tag{3.18}$$

one can hence write the commutator binary product in the form

$$(X|Y) = \{X|\hat{\Gamma}|Y\}, \tag{3.19}$$

where $\hat{\Gamma}$ takes the place of the metric operator $\hat{G}$. We note that, in (3.18), the upper sign holds for bosons and the lower for fermions. It is easily checked that, in the HS binary product, one has

$$(X|Y) = \{X|\hat{\Gamma}Y\} = \{\hat{\Gamma}X|Y\}, \tag{3.20}$$

i.e., the superoperator $\hat{\Gamma}$ is self-adjoint in this representation:

$$\hat{\Gamma}^{\ddagger} = \hat{\Gamma}. \tag{3.21}$$

It is obvious that this metric is not always positive definite and, if the "killer condition" (1.65) is satisfied, one obtains $(D|D) = \pm\langle\phi|D^{\dagger}D|\phi\rangle$.

If the self-adjoint metric superoperator $\hat{G}$ in (3.2) is not positive definite but has an inverse $\hat{G}^{-1}$, one speaks of an *indefinite metric* and, even in this case, adjoint operators are related through the relation (3.6). However, if the superoperator $\hat{G}$ has the eigenvalue zero, one speaks of a *degenerate metric* and the corresponding binary product is said to be degenerate. In such a case, the inverse superoperator $\hat{G}^{-1}$ does not exist, and the relation (3.6) breaks down, indicating that the concept of adjoint operators may lose its original meaning for a degenerate binary product. In such a case, even the bivariational principle (3.15) may break down.

In a *nondegenerate metric,* the validity of the relation $[A|B] = 0$ for all operators A should necessarily imply $B = 0$. Starting from the definition $[A|B] = \{A|\hat{G}|B\}$ and putting $A = \hat{G}B$, one obtains $\|\hat{G}B\|^2 = 0$, which implies

$$\hat{G}B = 0. \tag{3.22}$$

Only in the case when the superoperator $\hat{G}$ has an inverse $\hat{G}^{-1}$ can one draw the conclusion $B = 0$. If $\hat{G}$ has an eigenvalue zero, the relation (3.22) is fulfilled for any eigenoperator B associated with this particular eigenvalue.

As mentioned previously, Goscinski[24] and his co-workers have pointed out that the binary product $(X|Y)$ is *degenerate* in the sense that, if $(X|Y) = 0$ for all X, one cannot draw the conclusion $Y = 0$. Instead one obtains

$$\hat{\Gamma}Y = \Gamma Y \pm Y\Gamma = 0; \tag{3.23}$$

in the case of the lower sign, this relation is, of course, fulfilled for the operator $Y = \Gamma$. Let us now try to determine all nontrivial solutions $Y \neq 0$ to the eigenvalue relation $\hat{\Gamma}Y = 0$, and it is then convenient to distinguish between the two signs.

In the case of the *upper sign,* one has

$$\Gamma Y = -Y\Gamma. \tag{3.24}$$

Multiplying this relation to the left and right by Γ and observing that $\Gamma^2 = \Gamma$, one obtains

$$\Gamma Y = -\Gamma Y\Gamma, \qquad \Gamma Y\Gamma = -Y\Gamma, \tag{3.25}$$

i.e.,

$$\Gamma Y = Y\Gamma = 0. \tag{3.26}$$

Since $\Gamma = |\phi\rangle\langle\phi|$, it is evident that, if $\phi = \phi_1$ is considered as the first function in an orthonormal basis, then the general solution to (3.26) has the form

$$Y = \sum_{k,l=2}^{\infty} |\phi_k\rangle Y_{kl}\langle\phi_l|. \tag{3.27}$$

In the case of the *lower sign*, one has instead

$$\Gamma Y = Y\Gamma, \tag{3.28}$$

or $|\phi\rangle\langle\phi|Y = Y|\phi\rangle\langle\phi|$. Multiplying this relation to the right by $|\phi\rangle$, one obtains

$$Y\phi = \phi\langle\phi|Y|\phi\rangle = \phi\lambda, \tag{3.29}$$

which relation is valid for all operators Y having ϕ as an eigenfunction. The general solution to (3.28) takes in such a case the form:

$$Y = \lambda\Gamma + \sum_{k,l=2}^{\infty} |\phi_k\rangle Y_{kl}\langle\phi_l|. \tag{3.30}$$

The CBP binary product is hence highly degenerate.

It should be remembered, however, that this binary product was tailored to fit the current propagator theory which was essentially based on the expression (1.53). This gives

$$\begin{aligned} I_1 &= (C|\hat{L}C)/(C|C) = \{C|\hat{\Gamma}\hat{L}C\}/\{C|\hat{\Gamma}C\} = \{\hat{\Gamma}C|\hat{L}C\}/\{\hat{\Gamma}C|C\} \\ &= \{C_1|\hat{L}C\}/\{C_1|C\}, \end{aligned} \tag{3.31}$$

where we have introduced the notation

$$C_1 = \hat{\Gamma}C = \Gamma C \pm C\Gamma. \tag{3.32}$$

The last member of (3.31) is a typical bivariational expression, but—since the Liouvillian $\hat{L}$ is self-adjoint—one should expect that the bivariational principle (3.15) should lead to a solution, where C_1 is proportional to C. This is usually not the case, unless some specific conditions are satisfied, and one is hence facing about the same problems as discussed before in connection with the quantity I_1, and one may then resort to the methods developed in Section II.

D. Some Aspects on the Special Propagator Theories and the EOM Method

The commutator binary product introduced by Goscinski and coworkers was chosen so that the special propagators in the Linderberg–Öhrn theory[17] could be written explicitly in the form (1.56). Using the connection formula (3.19), one hence obtains

$$\langle\langle A; B\rangle\rangle_z = \{A|\hat{\Gamma}\hat{R}(z)|B\}, \tag{3.33}$$

which defines the propagator in terms of the Hilbert–Schmidt binary product. Using the expansion theorem (1.39), one now finds that this propagator satisfies the relation

$$\langle\langle A; B\rangle\rangle_z = z^{-1}\{A|\hat{\Gamma}B\} + z^{-1}\langle\langle A; \hat{L}B\rangle\rangle_z \tag{3.34}$$

in agreement with (1.40).

It is evident that one may introduce a slightly more general propagator by means of the more general binary product defined by (3.2), and one may start from the formula

$$\langle\langle A; B\rangle\rangle_z = [A|\hat{R}(z)|B] = \{A|\hat{G}\hat{R}(z)|B\}, \tag{3.35}$$

where $\hat{G}$ is the metric superoperator. Such a propagator satisfies the expansion formula

$$\langle\langle A; B\rangle\rangle_z = z^{-1}\{A|\hat{G}|B\} + z^{-1}\langle\langle A; \hat{L}B\rangle\rangle. \tag{3.36}$$

In principle, such a propagator theory would be particularly simple if the metric superoperator $\hat{G}$ satisfies the extra conditions (3.3). In practice, one has found it algebraically and computationally convenient to choose $\hat{G} = \hat{\Gamma}$, and the question is whether one could further simplify the theory by introducing *multicommutator* superoperators $\hat{G}$. In all events, it may be worthwhile to investigate whether there would be any better choice of the metric superoperator $\hat{G}$.

The key problem in the Liouvillian formalism is not only the direct solution of the eigenvalue problem (1.22) in the operator space but also—in the case of *degenerate* eigenvalues ν—the separation of the eigenelements into components having the form of "excitation operators" of the special type (1.23) associated with specific initial and final states. Letting the superoperator $\hat{G}$ work on (1.22), one obtains

$$\hat{G}(\hat{L} - \nu \cdot \hat{1})C = 0, \tag{3.37}$$

and, if $\hat{G}$ has an inverse $\hat{G}^{-1}$, one can then go back to the original eigenvalue problem. Let us further assume that $\hat{G}$ satisfies the additional conditions (3.3), so that the binary product $[A|B] = \{A|\hat{G}|B\}$ is positive definite. Introducing a basis $\mathbf{B} = \{B_r\}$ in the operator space, we will now consider a series of conditions

$$[B_r|(\hat{L} - \nu \cdot \hat{1})D] = 0, \tag{3.38}$$

for $r = 1, 2, 3, \ldots$. Multiplying these conditions by the coefficients a_r^*, summing over r, and introducing the special operator

$$\Theta = \sum_r B_r a_r, \tag{3.39}$$

one obtains the relation

$$[\Theta|(\hat{L} - \nu \cdot \hat{1})D] = 0, \tag{3.40}$$

for arbitrary operators Θ, which implies that $(\hat{L} - \nu \cdot \hat{1})D = 0$ according to axiom 4. If on the other hand, the conditions (3.38) are valid only for a truncated basis with $r = 1, 2, 3, \ldots, m$, then D is an approximate eigenelement to the Liouvillian. If one expands D in the form $D = \sum_s B_s d_s$, the conditions (3.38) correspond to a system of linear equations

$$\sum_s [B_r|\hat{L} - \nu \cdot \hat{1}|B_s]\, d_s = 0, \tag{3.41}$$

or

$$\sum_s (L_{rs} - \nu \cdot \Delta_{rs})\, d_s = 0, \tag{3.42}$$

with the secular equation $|L_{rs} - \nu\Delta_{rs}| = 0$ of order m. Here the Liouvillian and metric matrices have the following forms, respectively:

$$L_{rs} = [B_r|\hat{L}|B_s] = \{B_r|\hat{G}|\hat{L}B_s\} = \mathrm{Tr}\, B_r^\dagger[\hat{G}(HB_s - B_sH)], \tag{3.43}$$

$$\Delta_{rs} = [B_r|B_s] = \{B_r|\hat{G}|B_s\} = \mathrm{Tr}\, B_r^\dagger(\hat{G}B_s). \tag{3.44}$$

Putting $\Theta = D$ into the relation (3.40), one gets an approximation for the eigenvalue ν in the form:

$$I_3 = [D|\hat{L}|D]/[D|D]. \tag{3.45}$$

It is evident that, as long as the metric superoperator $\hat{G}$ satisfies the conditions (3.3), this is a legitimate approach for solving the original eigenvalue problem (1.22).

In the special propagator theories and the EOM method, one is using a formalism which is equivalent with the use of a metric superoperator $\hat{G} = \hat{\Gamma}$ defined in (3.18) which is by no means positive definite and which lacks an inverse. This means that all the relations (3.37)–(3.45) shift character and become only *necessary* conditions, which permit also other types of solutions to occur.[13] It is easily checked that, in this case, the Liouvillian and metric matrices take the form:

$$\begin{aligned} L_{rs} &= \mathrm{Tr}\ B_r^\dagger[\hat{\Gamma}(\hat{L}B_s)] = \mathrm{Tr}\ B_r^\dagger[\Gamma(\hat{L}B_s) \pm (\hat{L}B_s)\Gamma] \\ &= \mathrm{Tr}\ \Gamma[(\hat{L}B_s)B_r^\dagger \pm B_r^\dagger(\hat{L}B_s)] = \langle\phi|[(\hat{L}B_s); B_r^\dagger]_\pm|\phi\rangle, \end{aligned} \tag{3.46}$$

$$\begin{aligned} \Delta_{rs} &= \mathrm{Tr}\ B_r^\dagger[\hat{\Gamma}B_s] = \mathrm{Tr}\ B_r^\dagger(\Gamma B_s \pm B_s\Gamma) \\ &= \mathrm{Tr}\ \Gamma(B_sB_r^\dagger \pm B_r^\dagger B_s) = \langle\phi|[B_s; B_r^\dagger]_\pm|\phi\rangle, \end{aligned} \tag{3.47}$$

respectively, and that—except for the order in the $[;]_\pm$ commutator—these expressions agree with (2.81) and (2.82) as well as with the matrices occurring in the original equations (1.49). It is hence possible to derive the basic equations in the EOM method by the metric superoperator $\hat{\Gamma}$.

E. The GNS Binary Product

In the theoretical studies of various operator spaces, it is—of course—particularly convenient to work with such spaces which are realizations of the abstract Hilbert space in the sense of von Neumann.[1] In the discussions of the special propagator methods, such a Hilbert space has been introduced by Weiner and Goscinski[30] through the Gelfand, Naimark, and Siegel (GNS) construction.[31] If Γ is the system operator under consideration satisfying the relations (1.3), the GNS space $\{X\}$ has the binary product

$$(X|Y)_\Gamma = \{X\Gamma^{1/2}|Y\Gamma^{1/2}\} = \mathrm{Tr}\ \Gamma^{1/2}X^\dagger Y\Gamma^{1/2} = \mathrm{Tr}\ X^\dagger Y\Gamma = \langle X^\dagger Y\rangle_\Gamma, \tag{3.48}$$

and it satisfies hence all the four axioms of a positive binary product, except that it is degenerate if Γ has some eigenvalues 0. In order to avoid this difficulty, the elements of the proper Hlbert space were chosen as *equivalence classes;* two operators X_1 and X_2 are said to be "equivalent," if $(X_1 - X_2|Y)_\Gamma = 0$ for all Y, which also implies $(X_1 - X_2|X_1 - X_2)_\Gamma = 0$. This is analogous with the construction of the ordinary L^2 Hilbert space $\{\Psi\}$, where the elements are also equivalence classes; two wave functions Ψ_1 and Ψ_2 are said to be "equivalent," if $\langle\Psi_1 - \Psi_2|\Phi\rangle = 0$ for all Φ, i.e., if $\|\Psi_1 - \Psi_2\|^2 = \langle\Psi_1 - \Psi_2|\Psi_1 - \Psi_2\rangle = 0$.

It should be observed that the GNS space $\{X\}$ contains the Hilbert–Schmidt space as a subspace, but also that it is considerably larger, since it is now sufficient to require that the product $X\Gamma^{1/2}$ should be a Hilbert–Schmidt operator. As an example, we note that the identity operator 1 belongs to the GNS space but not to the HS space. By using (3.17) and (3.48), one may now write the commutator binary product $(X|Y)$ in the form:

$$(X|Y) \equiv (Y^\dagger|X^\dagger)_\Gamma \pm (X|Y)_\Gamma, \tag{3.49}$$

and it is then possible to discuss the special propagator theories and the double-commutator EOM method in terms of the GNS Hilbert space. It should be observed, however, that the Liouvillian superoperator $\hat{L}$ is usually not self-adjoint with respect to the binary product (3.48), except for very special reference states Γ. This follows from the fact that

$$\begin{aligned}(\hat{L}X|Y)_\Gamma - (X|\hat{L}Y)_\Gamma &= \mathrm{Tr}[(X^\dagger H - HX^\dagger)Y\Gamma - X^\dagger(HY - YH)\Gamma \\ &= \mathrm{Tr}\, X^\dagger Y(H\Gamma - \Gamma H) = \{X^\dagger Y|(H\Gamma - \Gamma H)\}, \quad (3.50)\end{aligned}$$

where the last member is vanishing for arbitrary operators X and Y, if and only if $H\Gamma = \Gamma H$, i.e., if the reference operator Γ reduces the Hamiltonian and represents a *stationary state*. If this is really the case, one has, of course, already partly solved the Hamiltonian eigenvalue problem exactly, which is indeed very seldom the case for a true many-body Hamiltonian. In order to investigate whether the various expectation values of the Liouvillian $\hat{L}$ are real or not, one may then have to rely on very special procedures.

The commutator binary product defined through (1.54) or (3.17) and the GNS binary product (3.48) have played an important role in revealing the mathematical structure of the special propagator methods and their connection with the EOM approach. In the opinion of the author, however, it is of great advantage to work with a binary product with respect to which the Liouvillian superoperator $\hat{L}$ from the very beginning is *self-adjoint,* and the HS binary product (2.2) would then be the most natural starting point.

F. Discussion

There is little question that the double-commutator expressions in (3.46) and (3.47) greatly simplify the algebraic and computational aspects of the calculation of the m^2 matrix elements occurring in the equation system (3.42); see Ref. 9. The theoretical results as to excitations, ionizations, etc., of certain many-particle systems are in such good agreement with experimental experience that one can probably only expect that part of this agreement will be lost, if one tries to refine the theory.

Still the purpose of this article is to advocate that the time is now ripe to attack the Liouvillian eigenvalue problem $\hat{L}C = \nu C$ directly in terms of *single-commutator* methods and secular equations of the type (2.16). This approach should further be combined with *ket–bra methods* of the type developed in Section II in order to decompose the eigenelements C associated with *degenerate* eigenvalues ν into components having the form of excitation operators of the type $C = |\Psi_f\rangle\langle\Psi_i|$.

In principle, it should be simpler to use the Hilbert–Schmidt binary product than the commutator binary product (1.54), since the former is positive definite and nondegenerate and makes the Liouvillian $\hat{L}$ a self-adjoint superoperator. This should apply particularly to the *inner projections* of a superoperator $\hat{M}$ having the inverse $\hat{M}^{-1}$, which are defined through the relations [cf. (1.60) and (1.61)]:

$$\hat{M}'_m = |\mathbf{B}\}\{\mathbf{B}|\hat{M}^{-1}|\mathbf{B}\}^{-1}\{\mathbf{B}|, \tag{3.51}$$

where $\mathbf{B} = \{B_1, B_2, \ldots, B_m\}$ is a truncated basis of order m in the operator space. It has been shown[32] that the inner projections $\hat{M}'_m$ converge toward the superoperator $\hat{M}$, when $m \to \infty$ and the set $\mathbf{B}$ becomes complete. Instead of the Liouvillian eigenvalue problem (1.22), it may then be more rewarding to study the eigenvalue problem (1.35) for the superresolvent $\hat{R}(z) = (z \cdot \hat{1} - \hat{L})^{-1}$ which—for $|z - \nu| \geq \rho$—is a bounded superoperator with much richer properties than the Liouvillian itself. This problem will be discussed in a forthcoming paper.

In addition to the superresolvent, it may be worthwhile to study propagators of the type (3.34):

$$\langle\langle A; B\rangle\rangle_z = \{A|\hat{G}\hat{R}(z)|B\} \tag{3.52}$$

in closed or expanded form, where it is possible to approximate the superresolvent $\hat{R}(z)$ to any accuracy desired by means of inner projections:

$$\hat{R}'_m(z) = |\mathbf{B}\}\{\mathbf{B}|z \cdot \hat{1} - \hat{L}|\mathbf{B}\}^{-1}\{\mathbf{B}|. \tag{3.53}$$

There are apparently many possibilities, and the problem is to improve the theory without increasing the volume and complexity of the calculations involved beyond the level which can be handled by the algebraic and computational tools available today.

It should be observed that, even if the Hilbert–Schmidt binary product is a natural device for the study of superoperators and is frequently treated in the mathematical literature, its use in propagator theory has been limited to a few papers, e.g., the development of a Liouvillian perturbation theory by Dalgaard and Simons.[33] This is hence a rather unexplored field, and only further studies may reveal how powerful this approach may be.

In conclusion, a few words should be said about the equivalence between the ket–bra formalism frequently used in this article and the particle–hole formalism based on the ideas of "second quantization" commonly used in the special propagator theories and the EOM method. Both formalisms are used to construct a basis for the operator space, and the essential difference is that the latter treats particles having specific symmetry properties—i.e., fermions or bosons—whereas the former is not yet adapted to any particular symmetry. In order to get a connection between the two schemes, it may be convenient in the ket–bra formalism to introduce a so-called *Fock space* for different numbers of particles

$N = 1, 2, 3, \ldots$ as a carrier space and to construct the basic wave functions φ_k as products of one-particle functions. A "fermion Fock space" is then obtained by taking the antisymmetric projection, whereas a "boson Fock space" is obtained by the symmetric projection. It should be observed, however, that it is sometimes convenient to deal with spaces with "mixed" or undefined symmetries, which occur in connection with the study of Hamiltonians of the type:

$$H = H_{(0)} + \sum_i \lambda_i H_i + \sum_{i<j} \lambda_{ij} H_{ij} + \sum_{i<j<k} \lambda_{ijk} H_{ijk} + \cdots, \tag{3.54}$$

where the quantities $\lambda_i, \lambda_{ij}, \lambda_{ijk}, \ldots$ are "interaction parameters" which may assume arbitrary values (including zero). Such Hamiltonians are of importance in studying linked-cluster theorems and size-consistency properties, but, since they are not invariant under permutations of the particle indices, they lack the standard symmetry properties, except in the special case when they all become equal (= 1). The study of such Hamiltonians requires hence a carrier space without any special symmetry built in, using, e.g., Hartree products of one-particle functions. It should be observed that the method of "second quantization" may be extended also to such a general product space.

Using the equivalence between the ket–bra formalism and the particle–hole operator method, it should be possible to take over some of the theorems formulated in the former to the latter, and vice versa. Research along these lines ought to give some very fruitful results and perhaps give a deeper insight also into the general propagator theory.

Appendix A. Some Rules for Ket–Bra Operators

For the convenience of the readers, some rules as to the treatment of ket–bra operators have been collected in this appendix. According to Dirac,[3] the binary product $\langle a|b\rangle$ in the wave function space $\{\Psi\}$ may be considered as the product of a bra-vector $\langle a|$ and a ket-vector $|b\rangle$. Introducing the ket–bra notation $T = |b\rangle\langle a|$, it symbolizes an operator T defined through the relation:

$$T\Psi = b\langle a|\Psi\rangle. \tag{A.1}$$

For the adjoint $T^\dagger$ defined through the formula $\langle T\Psi_1|\Psi_2\rangle = \langle \Psi_1|T^\dagger\Psi_2\rangle$, one gets directly $T^\dagger = |a\rangle\langle b|$. Since $T^2 = |b\rangle\langle a|b\rangle\langle a| = \langle a|b\rangle T$, the operator T satisfies the reduced Cayley–Hamilton equation

$$T(T - \langle a|b\rangle \cdot 1) = 0, \tag{A.2}$$

which means that T has the eigenvalues $\lambda = 0$ and $\lambda = \langle a|b\rangle$. The latter is associated with the eigenfunction b, and it is nondegenerate due to the fact that, if c would be another eigenfunction, the relation $Tc = \lambda c$ would give $b\langle a|c\rangle = \langle a|b\rangle c$, i.e., $c \sim b$. Hence $\lambda = \langle a|b\rangle$ with the multiplicity 1 is the only nonvanishing eigenvalue, and one obtains

$$\mathrm{Tr}\, T = \langle a|b\rangle. \tag{A.3}$$

In summary, one hence has the relations

$$[|b\rangle\langle a|]^\dagger = |a\rangle\langle b|, \qquad \mathrm{Tr}|b\rangle\langle a| = \langle a|b\rangle. \tag{A.4}$$

For a more extensive treatment of the ket–bra operators in general, the reader is referred to Refs. 2 and 4.

Appendix B. The Order of Linear Independence of Certain Operator Bases

Let us start by considering a truncated basis $\mathbf{B}$ in the operator space which contains m linearly independent elements $\mathbf{B} = \{B_1, B_2, \ldots, B_m\}$, and let ϕ be the reference function associated with the reference operator $\Gamma = |\phi\rangle\langle\phi|$. In order to determine the number of linearly independent elements in the product basis $\mathbf{B}\Gamma$, we will consider the functions

$$\phi_r = B_r \phi, \tag{B.1}$$

for $r = 1, 2, 3, \ldots, m$. In order to determine the number p of linearly independent elements in the set $\{\phi_r\}$, one may carry out a Schmidt's successive orthonormalization procedure, which leads to a set $\varphi = \{\varphi_k\}$ of order p, where $p \leq m$. Another way is to study the Gramm's determinant:

$$|\Delta_{rs} - \mu\delta_{rs}| = 0, \tag{B.2}$$

which has exactly p nonvanishing eigenvalues μ; here $\boldsymbol{\Delta} = \{\Delta_{rs}\}$ with $\Delta_{rs} = \langle\phi_r|\phi_s\rangle$ is the metric matrix.

Let us now consider the product basis $\overline{\mathbf{B}} = \mathbf{B}\Gamma$ having the elements $\overline{B}_r = B_r\Gamma = B_r|\phi\rangle\langle\phi| = |\phi_r\rangle\langle\phi|$. For the Hilbert–Schmidt binary product of these elements, one obtains

$$\{\overline{B}_r|\overline{B}_s\} = \mathrm{Tr}\, \overline{B}_r^\dagger B_s = \mathrm{Tr}|\phi\rangle\langle\phi_r|\phi_s\rangle\langle\phi| = \langle\phi|\phi\rangle\langle\phi_r|\phi_x\rangle = \Delta_{rs}, \tag{B.3}$$

i.e., the metric matrix $\{\overline{B}_r|\overline{B}_s\}$ has also exactly p nonvanishing eigenvalues, and the basis $\mathbf{B} = \mathbf{B}\Gamma$ is of order p.

It is further clear that the basis $\{\mathbf{B}\Gamma, \Gamma\}$ is of order p, if the reference function ϕ may be expanded in terms of the set $\{\phi_r\}$; otherwise, it is of order $(p + 1)$.

A general truncated operator basis $\mathbf{B}$ is usually not closed under adjunction (†), and this means that the adjoint basis $\tilde{\mathbf{B}}^\dagger = \{B_1^\dagger, B_2^\dagger, \ldots, B_m^\dagger\}$ may contain elements, which do not belong to the space spanned by the basis $\mathbf{B}$. In order to determine the order of the basis $\{\mathbf{B}\Gamma, \tilde{\mathbf{B}}^\dagger\Gamma\}$, we will now consider the set of wave functions

$$\{B_r\phi, B_r^\dagger\phi\}, \tag{B.4}$$

and if this set is of order p_1, the operator basis has the same order. Usually one has $p_1 > p$, and only if the space spanned by the set $\mathbf{B}$ is closed under adjunction (†), one gets $p_1 = p$.

Let us now study the ket–bra operators $|\tilde{\mathbf{\Phi}}\rangle\langle\mathbf{\Phi}|$ formed from the wave functions $\mathbf{\Phi} = \{\mathbf{B}\phi, \mathbf{B}^\dagger\phi\}$. One knows that, if one goes over to the corresponding orthonormal basis φ of order p_1, the associated ket–bra basis $|\varphi\rangle\langle\varphi|$ in the operator space (which is orthonormal in terms of the Hilbert–Schmidt binary product) is of order $p_1 \times p_1 = p_1^2$. One has further

$$|\tilde{\mathbf{\Phi}}\rangle\langle\mathbf{\Phi}| = |\tilde{\mathbf{B}}\phi, \mathbf{B}^\dagger\phi\rangle\langle\mathbf{B}\phi, \tilde{\mathbf{B}}^\dagger\phi| = \begin{pmatrix} \tilde{\mathbf{B}}\Gamma\tilde{\mathbf{B}}^\dagger; & \tilde{\mathbf{B}}\Gamma\mathbf{B} \\ \mathbf{B}^\dagger\Gamma\tilde{\mathbf{B}}^\dagger; & \mathbf{B}^\dagger\Gamma\mathbf{B} \end{pmatrix}, \tag{B.5}$$

which relation shows that the four matrices in (2.31) contain exactly p_1^2 linearly independent elements. This result is also easily checked by forming the metric matrix of the operators (B.5) in the Hilbert–Schmidt space; it has the form of the direct product $\mathbf{\Delta} \otimes \mathbf{\Delta}$; it has hence exactly p_1^2 nonvanishing eigenvalues.

If finally it is uncertain whether the reference operator Γ belongs to the space spanned by the basis $\{\mathbf{B}\Gamma, \tilde{\mathbf{B}}^\dagger\Gamma\}$ or not, it may be convenient to study the new basis $\{\mathbf{B}\Gamma, \tilde{\mathbf{B}}^\dagger\Gamma, \Gamma\}$ and the associated set of wave functions

$$\mathbf{\Phi} = \{\mathbf{B}\phi, \tilde{\mathbf{B}}^\dagger\phi, \phi\}, \tag{B.6}$$

which now contains p_2 linearly independent elements; one has $p_2 = p_1$, or $p_2 = p_1 + 1$, depending on whether the reference function ϕ may be expanded in terms of the basis (B.4) or not. In the latter case, the set of ket–bra operators $|\tilde{\mathbf{\Phi}}\rangle\langle\mathbf{\Phi}|$ is of the form

$$|\tilde{\mathbf{\Phi}}\rangle\langle\mathbf{\Phi}| = |\tilde{\mathbf{B}}\phi, \mathbf{B}^\dagger\phi, \phi\rangle\langle\mathbf{B}\phi, \tilde{\mathbf{B}}^\dagger\phi, \phi| = \begin{pmatrix} \tilde{\mathbf{B}}\Gamma\tilde{\mathbf{B}}^\dagger; & \tilde{\mathbf{B}}\Gamma\mathbf{B}; & \tilde{\mathbf{B}}\Gamma \\ \mathbf{B}^\dagger\Gamma\tilde{\mathbf{B}}^\dagger; & \mathbf{B}^\dagger\Gamma\mathbf{B}; & \mathbf{B}^\dagger\Gamma \\ \Gamma\tilde{\mathbf{B}}^\dagger; & \Gamma\mathbf{B}; & \Gamma \end{pmatrix}, \tag{B.7}$$

where the matrix (B.7) contains $p_2^2 = (p_1 + 1)^2 = p_1^2 + 2p_1 + 1$ linearly independent elements. It is evident that the submatrix of type (B.5) is of rank p_1^2, whereas the rectangular submatrix $(\Gamma\tilde{\mathbf{B}}^\dagger; \Gamma\mathbf{B})$ and its adjoint are each of rank p_1; the submatrix (Γ) is finally of rank 1.

The basis $\mathbf{B}^{(1)}$ consisting of the linearly independent elements in the matrices (B.7) has the interesting property that it is closed under adjunction (†) and multiplication, and that it contains the reference operator Γ, and it is hence a suitable starting point for the derivation of an approximate eigenelement D which has optimal properties and satisfies the algebraic conditions (1.32).

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