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THIN FILM OPTICAL SHUTTER

Final Report

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By
Sheldon L. Matlow

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SHELDON L. MATLOW, Ph.D.

THE SOUTHWALL CORP.
3961 E. Bayshore Rd.
Palo Alto, CA 94303

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PREFACE

This is the third in a series of Final Reports submitted on the Thin Film Optical Shutter (TFOS) project. The first Final Report included discussions of the thermodynamic limitations of TFOS, the quantum mechanical methods developed for calculating the dielectric constant and imaginary refractive index as a function of frequency for macroconjugated macromolecules (MCMM) and the thermochromic mechanisms which could be used for switching MCCM [1]. The second Final Report included discussions of additional quantum mechanical methods which had been developed and the results of calculations on polyynes and polyenes [2]. Where full development of the theory is not required for understanding results, equations from these Final Reports will be cited. Except for this limiation, this Final Report is self-contained. A specific embodiment of MCMM, the poly (p-phenylene)'s, has been chosen as the one most likely to meet all of the requirements of TFOS. The reason for this choice are included in this Report. In order to be able to make meaningful calculations of the thermodynamicc and optical properties of the poly (p-phenylene)'s a new quantum mechanical method was developed — Equilibrium Bond Length (EBL) Theory. Some results of EBL Theory are included in this Report.

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I. INTRODUCTION

A. REQUIREMENTS FOR PASSIVE THERMAL MODULATION

The earth receives energy from the sun at a rate estimated to be 5.4×10^{24} Joules·year^{-1}. This is about thirty thousand times the currently used sources of energy [3]. Even if only one thousandth of one percent of the solar energy is utilized, the sun could supply 30% of the present energy requirements. The present problem, therefore, is not that insufficient solar energy is available, but rather the available technology is inadequate for the task, especially when the economics of the available technology is considered. We are, however, on the verge of the development of adequate technology for the thermal modulation of buildings by means of solar energy.

There are logically three approaches for this thermal modulation. The first is by use of the photovoltaic effect to convert solar energy directly to electricity and the subsequent use of the electricity for the thermal modulation. In the other two approaches, respectively called 'active' and 'passive' modulation, the solar radiation is absorbed, converted to vibrational energy and re-emitted as infrared radiation. Prof. W.W.S. Charters of the University of Melbourne distinguishes between active and passive modulation by

> 'An active system ... (is) one in which it is essential to supply input energy in the form of electrical power or mechanical work in order to transfer the collected energy from the point of collection directly to the interior of the building or to an assigned thermal storage ... the basic feature of a passive system is that no input of energy is required to perform this transfer/storage task.' [4]

He then goes on to say,

> 'Because of their deceptive engineering simplicity little attention has been paid to the potential of passive heating systems, and engineers have favored the more complex active systems that are inherently more capable of regulation and control.' [5]

Finaly he declares,

> 'The basic problems to be overcome are those of thermal storage, which has to be designed into any such structure, and the associated fact of internal temperature control to achieve acceptable standards of temperature variation in the internal living quarters .... To assist with this control problem, one can use ventilation techniques in winter to reduce possibly unacceptable high temperatures and external shading devices in summer to prevent a larger proportion of the solar gain due to the large variation in the summer and winter solar angles.' [6]

The use of 'external shading devices' such as overhangs, bushes and trees has the disadvantage that they are not susceptible to feedback control. On a cloudy summer day they cannot be moved out of the way to permit more sunlight to enter the structure. Blinds and drapes require the intervention of a person, who may not be available at the appropriate time, or a thermostatically controlled motor, which requires the input of additional energy.

The ideal solution to the excessive solar gain problem is an 'optical shutter', a device which switches from being highly transmissive to solar radiation to being highly reflective to solar radiation when a critical temperature is reached in the enclosure. The switching occurs because one or more materials in the device undergo a phase transition at the critical temperature.

B. THIN FILM OPTICAL SHUTTER (TFOS)

A reasonable 'first guess' set of requirements for an optical shutter are:

1. The transition from the 'low' temperature state to the 'high' temperature state shall occur between 23° and 27°C (73.4° and 80.6°F);
2. In the 'low' temperature state the transmission of solar radiation shall exceed 80% of the incident radiation;
3. In the 'high' temperature state the reflection of solar radiation shall exceed 90% of the incident radiation;
4. In both states the absorption of solar radiation shall be less than 2% of the incident radiation; and
5. The system shall be chemically and photochemically stable in the presence of corrosives potentially present in the atmosphere and/or solar radiation in general and ultraviolet radiation in particular.

The traditional 'comfort zone' on room thermostats is given as 72° to 78°F. The range specified above is a little higher and a little broader than the 'comfort zone'. It is, however, sufficiently close to not be considered unreasonable. The second and third requirements are set to maximize solar gain when the room is 'cool' and to minimize solar gain when the room is 'warm'. The ultimate, but unrealizable, goal would be 100% transmission in the 'low' temperature state and 100% reflection in the 'high' temperature state. The values actually set are practical compromises.

Since the absorption of a significant proportion of the incident radiation by the optical shutter would cause the shutter to switch to the reflective state even though the room is too cool, it is essential that the shutter absorb less radiation than is necessary to cause self-switching. The 2% value is a 'guesstimate'. The maximum allowable absorptivity will have to be determined experimentally. In any case the absorptivity can be minimized by having the phase transition material in thin film form. Thus, we are logically led to TFOS, the Thin Film Optical Shutter.

C. THERMODYNAMIC REQUIREMENTS FOR TFOS

It has been found that the 80% transmissivity and the 90% reflectivity requirements force severe thermodynamic restrictions on optical shutters [7,8]. If each 'zone' in the shutter matieral which is in the lower temperature state contributed 100% to the transmissivity, and if each zone in the shutter material which is in the higher temperature state contributed 100% to the reflectivity, the maximum allowable value of the factor Q would be

$$Q = \left(\frac{N_2}{N_1}\right)_\ell = 20/80 = 0.25 , \qquad \text{(I-1)}$$

where

(I-2) N_1 = the number of 'zones' in the lower temperature state

N_2 = the number of 'zones' in the higher temperature state, and

= the 'lower' temperature, 23°C.

A 'zone' is an atom, a section of a molecule, or the entire molecule. If the shutter were exactly one 'zone' thick, equation (I-1) would apply, at best, only in the ideal case. Since the shutter cannot be expected to be exactly one 'zone' thick, we must require that the maximum allowable value of Q be considerably lower. If we also require that

$$Q = \left(\frac{N_1}{N_2}\right)_u \quad , \tag{I-3}$$

where

$$u = \text{the 'upper' temperature, } 27°\text{C} \quad , \tag{I-4}$$

the data of TABLE I-1 can be calculated. In making these calculations of the well-known thermodynamic functions

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{I-5}$$

and

$$N_2 = N_1 \exp(-\Delta G^o/Nk_oT) \tag{I-6}$$

TABLE I-1

Thermodynamic Analysis

of

TFOS Requirements

Q	ΔG^{o}_{ℓ} Joules·mole^{-1}	ΔG^{o}_{u} Joules·mole^{-1}	ΔS^{o} Joules·mole^{-1}·deg^{-1}
10^{-1}	5.669×10^{3}	-7.476×10^{3}	3.28×10^{3}
10^{-2}	1.134×10^{4}	-1.322×10^{4}	6.140×10^{3}
10^{-3}	1.701×10^{4}	-1.897×10^{4}	8.994×10^{3}
10^{-4}	2.268×10^{4}	-2.471×10^{4}	1.185×10^{4}
10^{-5}	2.835×10^{4}	-3.046×10^{4}	1.470×10^{4}

$Q = (N_2/N_1)_{\ell} = (N_1/N_2)_u$

N_1 = number of 'zones' in the lower temperature state

N_2 = number of 'zones' in the upper temperature state

ℓ = the lower temperature, 23°C

u = the upper temperature, 27°C

ΔG^{o}_{a} = standard Gibbs free energy of transition at temperature a

ΔS^{o} = standard entropy of transition are used, where

G = the Gibbs free energy

T = the absolute temperature (°K)

P = the pressure

S = the entropy

$N = N_1 + N_2$, and

k_o = Boltzmann's constant, 1.38066×10^{-23} Joules·deg^{-1} ·molecule^{-1}.

The only way in which such very large values of ΔS^o can be generated is by electron delocalization. It should be noted that the breaking of a chemical bond generates about 10^2 Joules·mol^{-1}·deg^{-1} of entropy. Thus, a $Q = 10^{-1}$ would require the breaking of about 33 bonds per molecule! If a value of 7×10^3 Joules·mole^{-1}·deg^{-1} is taken as a nominal value for ΔS^o, and if the phase transition material is a semiconductor such as silicon, this value of ΔS^o requires the dislocalization of 15.377 electrons per atom. The ridiculousness of this number becomes apparent when one considers that silicon has only 14 electrons per atom. There is, however, a type of macromolecule for which such delocalization entropies are not unreasonable — the macroconjugated matromolecules.

D. MACROCONJUGATED MACROMOLECULES

A 'macromolecule' is a molecule consisting of a large number of atoms. A 'polymer' is a macromolecule which can be considered conceptually to be made up of identical or similar small molecules called 'mers'. If one permits the usage of referring to individual atoms as mers, then there is no distinction between a macromolecule and a polymer. A single plane in a graphite crystal is a macromolecule, but it is a polymer only if the individual carbon atoms are considered to be mers.

A molecule is said to be 'conjugated' if the structure of the molecule permits the interaction of π-bonds with adjacent π-bonds and/or localized p-electrons or d-electrons on adjacent atoms. A macromolecule is 'macroconjugated' if the conjugation extends over a large region of the molecule. A macromolecule of graphite is macroconjugated. A macromolecule of polystyrene is not macroconjugated. The benzene rings are conjugated individually, but there are no interring interactions intra-molecularly. Since 'macroconjugated macromolecule' is a rather cumbersome expression, we have abbreviated it as 'MCMM'. [As the inventors of this 'word' we envoke the privilege of also setting its rules of grammar. We hereby declare MCMM to be both singular and plural. Thus, we one one MCMM and many MCMM.]

When an MCMM is switched from localized π-bonding in a mer to totally delocalized π-bonding, a delocalizion entropy of 7×10^3 Joules$\cdot$mole$^{-1}\cdot$deg^{-1} or even 14×10^3 Joules$\cdot$mole$^{-1}\cdot$deg^{-1} can easily be attained. In TABLE I-2 are listed the number of delocalized electrons per mer which are required to generate these two values of ΔS^o on delocalization. Since polyenes, polyynes and poly (p-phenylene)'s have two, four and six delocalizable electrons per mer, respectively, it is clear that such MCMM with suitable switches are potential candidates for the optical shutter material. There are, however, potential problems

TABLE I-2

MCMM Matching of TFOS Thermodynamic Requirements

q (mers per molecule)	n (electrons per mer, $\Delta S^{o} = 7 \times 10^{3}$ Joules$\cdot$mole$^{-1}\cdot$deg^{-1})	n (electrons per mer, $\Delta S^{o} = 14 \times 10^{3}$ Joules$\cdot$mole$^{-1}\cdot$deg^{-1})
160	1.1	2.1
150	1.2	2.3
140	1.3	2.5
130	1.4	2.7
120	1.5	3.0
110	1.7	3.3
100	1.9	3.7
90	2.1	4.2
80	2.4	4.8
70	2.9	5.7
60	3.5	6.9
50	4.3	8.7
40	5.8	11.5
30	8.3	16.5
20	14.1	28.2
10	36.6	73.2

which must be considered with regard to the use of MCMM for optical shutters.

Even though thermodynamics predicts that a given MCMM will switch in the required temperature range it makes no prediction as to the rate at which the switching occurs. An MCMM which switches within seconds of reaching the transition temperature is quite valuable, but an MCMM which takes an hour to switch is worthless for an optical shutter. Since an MCMM switches by changing its geometry, it is necessary for adjacent molecules to 'get out of the way' for the switching to occur. Such a concerted reorganization in bulk material may be very slow. It is planned, therefore, that the first generation of optical shutters be TFOS for this reason as well as the potential absorption problem. The rate of reorganization in a film of MCMM of the order of 100×10^{-10} meters (100 Å) thick can be expected to be reasonably fast.

The second problem which must be considered relates to the requirement that the optical shutter be chemically and photochemically stable. The macromolecules which are used commercially at the present time are with few exceptions notoriously unstable in the presence of sunlight. A TFOS which is photochemically unstable in the presence of sunlight is of rather little utility. Fortunately, there are ways in which this problem can be circumvented. We shall discuss the stability problem in considerable detail when we treat the theory of poly (p-phenylene).

Macroconjugation also gives a macromolecule some rather unusual properties. The simplest molecule with a π-bond is ethene. There is one bonding π-orbital and one anti-bonding π^*-orbital. By Equilibrium Bond Length (EBL) theory, which we shall discuss in great detail in this

Report, the quantum numbers for these orbitals are -1.114 and +1.114, respectively. In butadiene the quantum numbers would be -1.114, -1.114, +1.114 and +1.114 if the π-bonds did not interact. For the fully planar molecule the quantum numbers are -1.618, -0.737, +0.737 and +1.618. For the <u>ten</u> double bond homolog the values are -1.943, ..., -0.223, +0.223, ..., +1.943, where '...' represents eight values. For the <u>fifty</u> double bond homolog the values are -1.965, ..., -0.083, +0.083, ..., 1.965; and for the <u>hundred</u> double bond homolog the values are -1.965, ..., -0.069, +0.069, ..., +1.965. Thus, the highest and lowest values of the quantum numbers reach a constant value. Similarly, the middle quantum numbers approach asymptotes. Thus, as the molecule becomes longer more and more energy levels are placed between the extreme values -1.965 and -0.069 for +0.069 and +1.965. Thus, the 'distance' between adjacent energy levels decreases. The π-orbital systems of the polyenes, thus, approach the condition referred to by the solid state physicists as 'bands'. There is a bonding π-band and an anti-bonding π*-band. The 'distance' between the top of the bonding π-band and the bottom of the anti-bonding π-band is the 'band gap'. Photons with an energy less than the band gap energy cannot be absorbed, whereas photons with an energy greater than the band gap energy can be absorbed. Since the number of electrons which can be promoted to energy levels in the anti-bonding π*-band by photons with energies greater than the band gap energy is quite large, these molecules have quite large absorptivities for these photons. As we shall show later large absorptivities yield high reflectivities when specular reflection is possible. Thus, the MCMM can yield quite high reflectivities.

If sections of the molecule can be made to change their geometries as the temperature changes, the MCMM can be made to switch between the microconjugated and macroconjugated states. Thus, the MCMM can be made to switch between low absorptivity (high transmissivity) to high absorptivity (high reflectivity) with an increase in temperature. This is, however, precisely the type of material behavior which is required for the fabrication of the optical shutter. We shall, therefore, now turn to a discussion of MCMM theory.

II. MCMM THEORY

A. SWITCHING MERS

An MCMM can be considered to be made up of two kinds of mers -- delocalizing mers and switching mers. The delocalizing mers must, of course, contain at least one π-bond. They may be linear such as the ethenic and ethynic linkages, cyclic such as the p-phenylenic linkage and polycyclic such as the 1,4-naphthalenic linkage. In addition the cyclic and polycyclic linkages may be heterocyclic. With respect to geometric variation the ethynic linkage is the simplest. There are no geometric variations which are possible. For the ethenic linkages cis- and trans-isomers are possible. For the cyclics and polycyclics rotational variations are possible.

The switching mers must undergo reversible geometric rearrangements with temperature in such a way that there is π-bond coupling in one arrangement but not in the other. A change in π-bond coupling in a molecule will result in a change in the spectrum of the molecule in the near ultraviolet or in the visible. The change of spectrum with a change in temperature is known as 'thermochromism' [9-12]. Three of the known mechanisms of thermochromism have been found to be potential candidates for the thermal switching mers. They are the keto-enol isomerism, spiro atom isomerism and restricted rotation about a carbon-carbon bond [13]. Since the fifth requirement for TFOS is chemical and photochemical stability, the first two thermochromic mechanisms are probably poor choices. Carbonyl groups are well-known as sites for photochemical attack. We are, therefore, left with the third mechanism.

Restricted rotation about a carbon-carbon bond is the cause of the 'optically active' biphenyls [14]. Since the p-phenylenic linkage can act as both the delocalizing mer and as the switching mer, poly (p-phenylene) is an ideal candidate for an initial MCMM for TFOS.

B. ABSORPTIVITY AND REFLECTIVITY

In addition to being able to switch at the specified temperature MCMM for TFOS must also have the required high reflectivity in the 'high' temperature state. We shall, therefore, now consider the properties necessary for high reflectivity and whether MCMM can have these properties.

The generalized vector wave equation may be written as [15]

$$\nabla^2 \vec{\Phi} - \frac{1}{c^2}\frac{\partial^2 \vec{\Phi}}{\partial t^2} = 0 \,, \tag{II-1}$$

a solution of which is

$$\vec{\Phi} = \vec{\Phi}_o \exp(-i \langle k|x\rangle) \,, \tag{II-2}$$

where

$$i = \sqrt{-1} \,, \tag{II-3}$$

$$\langle k| = \langle k_1, k_2, k_3, \frac{i\omega}{c}| \,, \tag{II-4}$$

$$|x\rangle = |x_1, x_2, x_3, ict\rangle \,, \tag{II-5}$$

and ω is the angular frequency of the wave. In terms of more traditional symbols

(II-6) $$\langle k|x\rangle = \vec{k}\cdot\vec{r} - \omega t\ .$$

$\vec{k}$ is the 'wave propagation vector'. The wave number, k_j, is related to the wave length by

(II-7) $$k_j = \frac{2\pi}{\lambda_j}\ .$$

The angular frequency, ω, is related to the frequency, ν, by

(II-8) $$\omega = 2\pi\nu\ .$$

Thus,

(II-9) $$\begin{aligned}\frac{\omega}{k_j} &= \frac{2\pi\nu}{(\frac{2\pi}{\lambda_j})}\\ &= \nu\lambda_j\\ &= c_j\ .\end{aligned}$$

If c_o is the speed of light in vacuum, an 'index of refraction' may be defined by

(II-10) $$n_j = \frac{c_o}{c_j}\ .$$

From (II-7)

(II-11)
$$k_j = \frac{2\pi\nu}{\lambda_j\nu}$$
$$= \frac{2\pi\nu}{c_j}$$
$$= \frac{2\pi n_j\nu}{c_o} ,$$

and (II-4) becomes

(II-12)
$$\langle k| = \frac{2\pi\nu}{c_o} \langle n_1, n_2, n_3, i| .$$

For convenience the direction of propagation may be taken as perpendicular to the surface of the material medium with x_3 as the direction of propagation. If should be understood that the equations below must be modified if the direction of propagation is <u>not</u> normal to the surface. Thus,

(II-13)
$$\langle k| = \frac{2\pi\nu}{c_o} \langle 0, 0, n_3\ i| ,$$

and (II-2) becomes

(II-14)
$$\Phi = \Phi_o \exp\left[\frac{2\pi i\nu}{c_o} (c_o t - n_3 x_3)\right] .$$

If there is attenuation (absorption) in the medium, then

(II-15)
$$\Phi^2(x_3) = \Phi^2(x_3 = 0)\ e^{-\beta x_3} ;$$

where β is the 'attenuation constant'. The function Φ is squared in (II-15) because it is the <u>energy</u> of the wave which is attenuated, and the energy is proportional to the square of the amplitude of the wave. The combination of (II-14) and (II-15) yields

$$(11\text{-}16) \qquad \Phi^2(x_3) = \Phi_o^2 \exp\left[\frac{4\pi i\nu}{c_o}(c_o t - n_3x_3)\right] \cdot \exp[-\beta x_3]$$

$$= \Phi_o^2 \exp\left[\frac{4\pi i\nu}{c_o}(c_o t - n_3x_3 - \frac{\beta c_o}{4\pi i\nu} x_3\right]$$

$$= \Phi_o^2 \exp\left[\frac{4\pi i\nu}{c_o}(c_o t - n_3x_3 + \frac{ic_o\beta}{4\pi\nu} x_3)\right]$$

$$= \Phi_o^2 \exp\left[\frac{4\pi i\nu}{c_o}(c_o t - [n_3 - iK_3]\, x_3)\right] ,$$

where

$$(\text{II-17}) \qquad K_3 = \frac{c_o\beta}{4\pi\nu} ,$$

is the imaginary part of the index of refraction. The real part of the dielectric constant is related to n and K by

$$(\text{II-18}) \qquad \varepsilon = n^2 - K^2 .$$

Let the subscripts 'i' and 't' represent the medium in which the <u>incident</u> ray is found and the medium in which the <u>transmitted</u> ray is found, respectively. The reflectivity of the interface is given by

(II-19)
$$R = \frac{(n_i-n_t)^2 + n_t^2 - \varepsilon_t}{(n_i+n_t)^2 + n_t^2 - \varepsilon_t}$$

[16]. If the incident ray medium is air, $n_i \doteq 1$. The subscripts are now superfluous, and (II-19) can be written as

(II-20)
$$R = \frac{1 - 2n + 2n^2 - \varepsilon}{1 + 2n + 2n^2 - \varepsilon} .$$

It should be noted from (II-18) that the maximum possible value for ε for a given value of n is $\varepsilon = n^2$.

From (II-20) we obtain

(II-21)
$$\frac{\partial R}{\partial \varepsilon} = \frac{-4n}{(1 + 2n + 2n^2 - \varepsilon)^2} ,$$

and

(II-22)
$$\frac{\partial R}{\partial n} = \frac{-4 + 8n^2 + 4\varepsilon}{(1 + 2n + 2n^2 - \varepsilon)^2} .$$

Since n is also positive, (II-21) is negative definite. By definition the maximum possible value of R is +1.00. Thus,

(II-23)
$$R \to +1.00 \quad \text{as} \quad \varepsilon \to -\infty .$$

From (II-22) we see that, if ε is large in magnitude and negative in sign, the slope is negative for all reasonable values of n. Thus, we have

$$R \rightarrow +1.00 \quad \text{as} \quad n \rightarrow 0.00 \text{ for } \varepsilon \ll 0 \quad \text{(II-24)}$$

We shall consider an example of (II-24). Let $n = 0.1$ and $\varepsilon = -5$, then

$$R(n = 0.1, \varepsilon = -5) = 0.936 \quad \text{(II-25)}$$

Thus, we see that (II-24) is the guide to use for the attaining of the > 90% reflectivity for the upper temperature state. It should be noted <u>en passant</u> that (II-19) does not require that the highly reflective material be highly conductive (i.e., a <u>metal</u>). All that it requires is that the material be highly absorptive.

It will be instructive to examine the data for some specific metals. The data are all for <u>thin films</u> of the metals. The data are listed in TABLE II-1 through TABLE II-4. The 'white' metals aluminum and silver meet the reflectivity requirements quite well except around 4×10^{14} Hertz where aluminum is somewhat below specification. The 'yellow' metals, gold and copper are quite good until around 6×10^{14} Hertz where the reflectivity becomes poor. In all cases the failure occurs because the material is not sufficiently absorptive!

If a material is highly absorptive [β very large, or by (II-17), K very large] in the visible and the surface is rough, the material is <u>black</u>. If the surface is sufficiently smooth so that specular reflection occurs, the material is highly reflective. Thus, the 'blackness' of a material in bulk form can be taken as indicative of high reflectivity in smooth thin film form.

TABLE II-1

Optical Data for Aluminum

ν	n^a	k^a	ε^b	R^c
1×10^{14}	4.20	23.45	-532.26	98.0
2	1.92	12.90	-162.72	97.8
3	1.54	9.30	- 84.12	94.0
4	1.80	7.12	- 47.45	88.6
5	1.05	7.22	- 51.03	91.1
6	0.67	5.57	- 30.60	91.8
7	0.46	4.78	- 22.59	92.3
8	0.36	4.13	- 16.93	92.5

(a) Data taken in part from [17].

(b) Calculated.

(c) The data are experimental values and were not calculated by formula. The data were taken from [18].

TABLE II-2

Optical Data for Silver

ν	n^a	K^a	ε^b	R^c
1×10^{14}	1.38	20.30	-410.09	99.4
2	0.46	10.20	-103.92	99.4
3	0.25	6.81	- 46.32	99.4
4	0.08	5.05	- 25.49	99.1
5	0.06	3.75	- 14.06	98.6
6	0.05	2.87	- 8.24	97.9
7	0.06	2.22	- 4.95	96.5
8	0.05	1.80	- 3.24	91.7

(a) Data taken in part form [19].

(b) Calculated.

(c) The data are experimental values and were not calculated by formula. The data were taken from [18].

TABLE II-3

Optical Data for Gold

ν	n^a	K^a	ε^b	R^c
1×10^{14}	0.93	16.70	-278.03	99.3
2	0.42	8.39	- 70.21	99.1
3	0.31	5.58	- 31.04	98.6
4	0.14	4.27	- 18.21	97.4
5	0.20	2.90	- 8.37	91.9
6	0.84	1.84	- 2.68	47.7
7	1.40	1.83	- 1.37	38.7
8	1.41	1.68	- 0.84	37.4

(a) Data taken in part from [20].

(b) Calculated.

(c) The data are experimental values and were not calculated by formula. The data were taken from [18].

TABLE II-4

Optical Data for Copper

ν	n^a	K^a	ε^b	R^c
1×10^{14}	1.22	17.10	-290.91	98.6
2	0.51	8.76	- 76.45	98.6
3	0.20	6.27	- 39.27	98.5
4	0.16	4.46	- 19.87	97.9
5	0.19	2.98	- 8.85	93.3
6	0.88	2.42	- 5.09	60.0
7	0.87	2.11	- 3.71	52.1
8	1.07	2.13	- 3.37	43.8

(a) Data taken in part from [21].

(b) Calculated.

(c) The data are experimental values and were not calculated by formula. The data were taken from [18].

Since poly (p-phenylene) is the MCMM of choice for the thin film optical shutter, we shall continue our discussion of the theory of MCMM by discussing the theory of poly (p-phenylene).

III. POLY (p-PHENYLENE) THEORY

A. INTRODUCTION

Several objections can be raised against the use of poly (p-phenylene) for TFOS. Among these objections are

1. The inter-ring coupling in poly (p-phenylene) is too weak to provide the reflectivity required for the upper temperature state. In support of this claim one can cite
    - a. The polyphenyls are planar in their crystals,
    - b. They are colorless,
    - c. The limiting value for λ_{max} for the polyphenyl series is in the ultraviolet, and
    - d. The <u>black</u> poly (p-phenylene)'s are black because of impurities and/or cross linking.
2. The poly (p-phenylene)'s are too reactive to provide the required chemical and photochemical stability, and
3. The energies required to planarize non-planar poly (p-phenylene)'s are too great for use as TFOS switches.

We shall develop the theory of the poly (p-phenylene)'s in the context of replying to the above objections.

B. PLANARITY OF POLYPHENYLS

Although it is well known that the ortho-substituted polyphenyls and poly (p-phenylene)'s deviate from inter-ring coplanarity, it is widely believed that the unsubstituted compounds are inter-ring co-planar at least in the solid state. The argument given is that the intermolecular interactions in the crystal force the inter-ring co-planarity. In 1949

O. Bastiansen reported the dihedral angle for biphenyl in the vapor phase to be 40–45° [22]. The following year the value 45 ± 10° was reported [23]. Later the value 41.6 ± 2.0° was reported [24]. For a biphenyl solution in n-heptane Suzuki estimates the dihedral angle to be 19 – 23° [25].

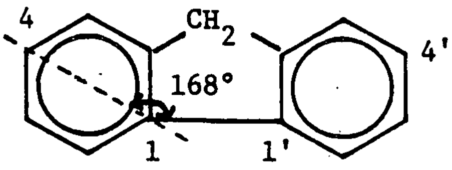
The early x-ray studies by Dhar indicated that the dihedral angle in crystalline biphenyl is exactly 0° [26]. A more recent study by Trotter reported the same value [27]. The same year, however, Robertson reported that the dihedral angle in crystalline biphenyl is 0.834° [28]. In recent years there have been published a series of papers on the crystal structures of various polyphenyls [29–35]. In each case double-well potentials are found for the various rings. For example, for p-terphenyl the central ring potential wells are at ± 13° at 200°K and 300°K [32]. The barrier height between the two wells is 0.65 kcal·mole^{-1} and 0.54 kcal·mole^{-1}, respectively, for the two temperatures.

Noren and Stille [36] report that EPR spectra of polyphenylene show that electrons are delocalized over a few (three to five) benzene rings. If we assume that the plane of each ring is 13° off of the plane of the previous ring and that the twists are all in the same direction, the sixth ring will be 65° off of the plane of the first ring. A non-coplanarity of 45° is probably sufficient to decouple the sixth from the first ring. Noren and Stille also report that NMR data on polyphenylene are consistent with the lack of inter-ring co-planarity [37]. Thus, it is clear that neither the polyphenyls nor the poly (p-phenylene)'s can be assumed to be totally co-planar in the solid at room temperature. We now turn to the question of inter-ring coupling when the rings are co-planar.

C. INTER-RING COUPLING

If a magnetic field is applied perpendicular to the plane of a closed ring conductor, an electric current will be induced in the conductor. The induced current has associated with it a magnetic field which opposes the impressed magnetic field. This is the 'standard' model for diamagnetism. In a molecule the 'ring circuits' will be around individual atoms except in the case of molecules such as benzene. If the magnetic field is perpendicular to the plane of the ring, the entire ring is the 'ring circuit' for the π-electrons. The difference between the sum of the atomic 'ring circuits' magnetic suceptibilities and the 'π-ring circuit' susceptibility is the anisotropy. For benzene the anisotropy is 54×10^{-6} [38]. If there is no inter-ring interaction for biphenyl, the corresponding value should be 108×10^{-6}. London's value, however, is 119×10^{-6}. Since there is no 'ring circuit' for the carbonate ion, the anisotropy would be expected to be identically zero. The experimental value however, is 4×10^{-6} [39]. The reason for these "excess" anisotropies has been shown to be that in the presence of the magnetic field the interaction between non-bonded atoms is much greater than would be expected by virtue of the value of the overlap integral [40].

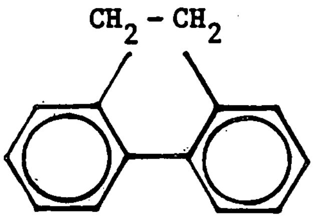
Wheland has reported the values of resonance energies for various compounds calculated from heats of combustion using the method of Klages and the method of Franklin [41]. For benzene the respective values are 36.0 and 36.4 kcal·mole^{-1}. For co-planar, non-interacting rings, one would expect for biphenyl the values 72.0 and 72.8 kcal·mole^{-1}, respectively. The values reported by Wheland for solid biphenyl, however, are 71.0 and 71.5 kcal·mole^{-1}, respectively. Thus, it would appear that not only do the rings not interact, but that planarization requires an expenditure of 1.0 - 1.3 kcal·mole^{-1}. Fluorene can be considered to be a biphenyl molecule with an o, o'-methylene bridge. This bridge would be expected to force co-planarity of the two rings. The crystal structure of fluorene shows that this is the case except that the angle between the 1, 1' bond and the 1, 4 and 1',4' rays is 168° rather than the 0° found in biphenyl [42]. The resonance energies for fluorene



FLUORENE

reported by Wheland are 75.9 and 77.7 kcal·mole^{-1}, respectively. Thus, the 'excess' resonance energy of fluorene over twice the benzene value is 3.9 - 4.9 kcal·mole^{-1}. Again we find a significant inter-ring interaction when the rings are co-planar.

The rate at which molecular chlorination occurs in acetic acid for various biphenyls can be compared to that for benzene [43]. For methyl benzene, biphenyl and fluorene the relative rates are 356, 422, and 113,000, respectively. For 2, 2'-dimethyl diphenyl the relative rate drops to 292, whereas for 9, 10-dihydrophenanthrene the relative rate is 12,200. Whether the mechanism for this chlorination is free radical or electrophilic, it is to be expected that strong inter-ring interactions will increase the rates of the reactions. It should be noted that 9, 10- dihydrophenanthrene is not quite planar.



9,10- DIHYDROPHENENTHRENE

D. SPECTRA OF POLYPHENYLS AND POLYPHENYLENES

We shall discuss the three spectral objections together here. Both the data cited by Suzuki [44] and the data cited by Noren and Stille [45] indicate that the p-polyphenyls which have been studied are colorless in solution. These data are listed in TABLE III-1. The numbers listed are the values of λ, in nm, for the <u>lowest</u> energy peak observed. The calculated values were obtained by the use of Kuhn's 'root law' [46] which is obtained from the very simplest form of semi-empirical molecular orbital theory. The agreement between the theory and the experimental data is remarkable. There are, however, some serious difficulties which preclude one from accepting the 343.8 nm asymptote value for poly (p-phenylene).

TABLE III-1

Ultraviolet Spectra of p-Polyphenyls

Compound	λ_{max}, Ref 44	Observed, nm Ref. 45	λ_{max}, Calculated, nm Ref. 45
Benzene	203.0	-	-
Biphenyl	247.4	251.5	251.7
p-Terphenyl	276.5	280.0	280.0
p-Quaterphenyl	292.0	300.0	298.0
p-Quinquiphenyl	-	310.0	309.7
p-Sexiphenyl	308.0	317.5	317.6
p-Septiphenyl	-	-	323.1
p-Polyphenylene	-	-	343.8

The data cited by both Suzuki and by Noren and Stille are for solution and not for the solids. As we have indicated in SECTION III.B the dihedral angle for biphenyl in solution is around 20°. Thus, the theory is predicting the values of λ_{max} for non-planar molecules. For thin films of biphenyl Dale reports the existence of a 'hidden' band with the λ_{max} of 275 nm [47]. Furthermore, fluorene has a peak at about 300 nm as does 9, 10-dihydrophenanthrene although the extinction coefficient for the latter molecule is much smaller [48].

One could argue that the 'hidden' band is the result of a transition other than a π-π^* transition, or that it is a π-π^* transition which is forbidden. Since it is not reasonable for these types of molecules to assume that there are electronic transitions which are lower in energy than the least energetic of the π-π^* transitions, the first suggestion is not very probable. The second suggestion, however, does have merit and should be investigated. We, therefore, made our own analysis of the π-electronic structure of benzene and planar biphenyl. We assumed that all C-C bond lengths in planar biphenyl are the same as the C-C bond length in benzene. We did not, however, ignore adjacent atom overlap integrals as is the practice in the simple Hückel molecular orbital treatment. Furthermore, we ignored the energy required to planarize the biphenyl. Because of these approximations we do not have the right to assume that our calculation of transition energies will be very close to the observed transition energies. Whether a transition is allowed or forbidden is, however, a group theoretic matter, and group theoretic results are a function only of the symmetries assumed.

The relationship between the quantum numbers, λ_j, obtained from the secular determinant, and the π-orbital energy is given by

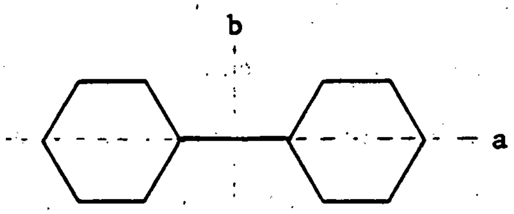
$$E_j = \frac{-\gamma\lambda_j}{1 - 0.2455\,\lambda_j}\,, \tag{III-1}$$

where γ is a modified exchange integral and is negative, and 0.2455 is the value for the overlap integral for adjacent $2p_\pi$-orbitals for carbon atoms in benzene. For benzene the highest occupied molecular orbital has the quantum number -1. The lowest unoccupied molecular orbital has the quantum number $+1$. Thus, we calculate a π-π^* transition energy for benzene of

$$\Delta E_g(\text{benzene}) = -2.128\gamma\ . \tag{III-2}$$

We obtain the value of γ by associating this transition with the 203 mμ peak of benzene.

The structure taken for biphenyl is



The lines a and b represent the symmetry planes for planar biphenyl. If the electric field vector is perpendicular to the b-plane, both rings are involved in absorption. The allowed transitions are

$$a,\tilde{b} \rightarrow a,b \qquad \text{and} \qquad a,b \rightarrow a,\tilde{b} \ ,$$

where $a,\tilde{b}$ represents an orbital which is symmetric with respect to the a-plane and anti-symmetric with respect to the b-plane. Similarly, a,b represents an orbital which is symmetric with respect to the a-plane and symmetric with respect to the b-plane. Other allowed transisions are

$$\tilde{a},\tilde{b} \rightarrow \tilde{a},b \qquad \text{and} \qquad \tilde{a},b \rightarrow \tilde{a},\tilde{b} \ .$$

The values of the quantum numbers of the various π-orbitals of planar biphenyl and their symmetries are listed in TABLE III-2. The $-0.705\ (a,\tilde{b}) \rightarrow +0.705\ (a,b)$ transition energy is

$$\Delta E_g(\text{biphenyl}) = -1.454\ \gamma \ . \qquad \text{(III-3)}$$

Using the value of γ obtained from the benzene calculation, we calculate a wavelength of 297.1 nm. This is remarkably close to the 300 nm value cited above for fluorene and 9, 10-dihydrophenanthrene. The crudeness of the approximations, however, preclude our expecting so close a correspondence. It should, however, be noted that this transition is the lowest in energy of all π-π^* transitions, allowed or forbidden. Thus, our calculations suggest, but do not in any way prove, that the asymptotic value for this transition in fully planarized poly (p-phenylene) is at a much lower energy than is believed at the present.

TABLE III-2

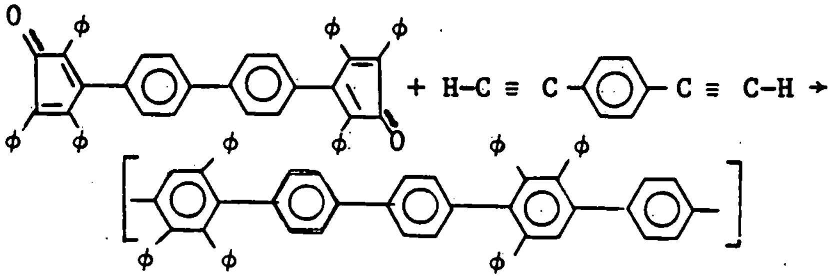
π-Orbitals, Planar Biphenyl

Quantum Number	Symmetry
+2.278	$a,\tilde{b}$
+1.891	a,b
+1.317	$a,\tilde{b}$
+1.000	$\tilde{a},b$
+1.000	$\tilde{a},\tilde{b}$
+0.705	a,b
-0.705	$a,\tilde{b}$
-1.000	$\tilde{a},\tilde{b}$
-1.000	$\tilde{a},b$
-1.317	a,b
-1.891	$a,\tilde{b}$
-2.278	a,b

If our hypothesis is correct that the 'band gap' for fully planarized poly (p-phenylene)'s is in the infrared and not in the ultraviolet, several 'color' phenomena should be observed for the poly (p-phenylene)'s.

1. Polyphenylenes which cannot be planarized because of steric hindrance should be colorless.
2. Polyphenylenes which can be fully planarized, but are not, should become darker when compressed. The compression energy will force the rings to assume a more co-planar configuration.
3. Fully planarized poly (p-phenylene)'s should be a shiny black, and
4. Derivatives of fully planarized poly (p-phenylene)'s which do not interfer with planarization should also be black. This requirement ensurs that the 'blackness' is not cause by impurities. It does not, however, guarantee that the 'blackness' is not caused by extensive cross-linking between chains.

By means of a Diels-Alder coupling the reaction



has been carried out [49]. Because of the pendant benzene rings the product cannot be planarized. It would, therefore, be expected to be colorless. Clear, colorless, films of the product have been cast from chloroform.

Grey to brownish black polymers have been synthesized by the anodic oxidation of benzene at the interface between benzene and anhydrous HF to which a small amount of water or KF was added [50]. Chemical analyses of the products indicate that they are polyphenylenes with some fluorine and some oxygen. In some cases the infrared spectra indicate that the linkages are para.

An attempt to produce a poly (arylene sulfone) by the Friedel-Crafts reaction of m-benzene-disulfonyl chloride and biphenyl in nitrobenzene yielded a *black* polyphenylene of a molecular weight of 3000 - 4000 Daltons [51]. The oxidative cationic polymerization of benzene with aluminum chloride and cupric chloride yields a brown product with no evidence of ortho, meta or non-aromatic linkages in the infrared spectrum [52]. On compression blue-black pellets were obtained.

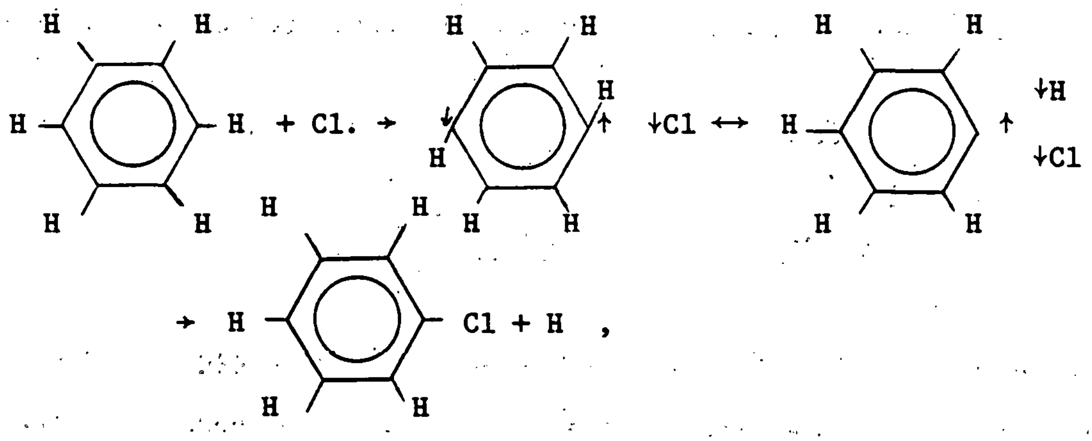
A poly (p-phenylene) of about 100 mers was obtained by the chlorination of poly (1, 3- cyclohexadiene) with subsequent dehydrochlorination [53]. A shiny black polymer of composition $(C_6H_{3.78}C\ell_{0.31})_n$ was obtained. The polymer was sulfonated with hot concentrated sulfuric acid. The polymer obtained was soluble in methanol and in concentrated sulfuric acid, and was also *black*. The method of synthesis and the chemical analysis preclude a significant amount of cross-linking. Furthermore, the color of the *soluble* sulfonated polymer indicates that the color is not the result of impurities.

E. CHEMICAL AND PHOTOCHEMICAL STABILITY

'The excellent resistance of poly (p-phenylene) and poly(phenylene) type polymers in general to oxidation, radiation, and thermal degradation is one of their most attractive characteristics,' [54] 'One of the most important properties of the polyphenylenes is their thermal stability ...' [55] . Thermal and thermo-chemical degradations are, however, not the same as photochemical degradations. The thermal degradations are initiated by exciting vibrational transitions, whereas photochemical degradations are initiated by exciting electronic transitions. In order to be justified in envoking thermal stability as proof of photochemical stability we must be able to show that the rate limiting step in the two types of degradation are the same.

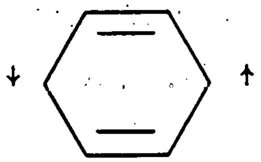
For degradation to occur either a bond must be directly broken or a new bond must be formed, the result of which is the breaking of a different bond. In the gas phase the combined kinetic energies of two colliding molecules can be sufficient to break a bond of one of the molecules. In the solid state such an event is not very likely. The kinetic energy of a gas phase molecule colliding with the surface is usually converted to a vibrational excitation which involves the vibrations of many atoms. The probability of the localization of the vibration is quite small. If the kinetic energy of the colliding molecule is sufficiently high, as is the case with plasma etching, an atom can be knocked out of the surface directly. Thus, neither in thermal, nor in photochemical degradations at the energies of interest here is there a significant probability that direct homolytic bond cleavage occurs.

A free radical reaction can occur with a benzene ring if an effectively localized π-electron can be produced in the activated complex. Thus,

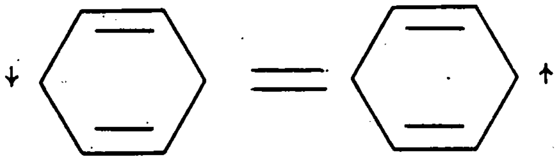


where the small arrows indicate electron spins. In this case the excitation is effectively to a singlet state. Conservation of angular momentum in the photon absorption case requires that the effectively localized π-electronic structure must be a triplet. The above reaction can be initiated in two ways. The approaching free radical can induce a polarization of the π-electron system or the π-electron system can by polarized first by the absorption of a photon or a phonon. Since the room temperature oxidation of of poly (p-phenylene)'s by oxygen is not observed, the presence of the oxygen biradical is not sufficient to induce polarization. Thus, the polarization must be induced by a phonon (thermal degradation) or by a photon (photochemical degradation).

For benzene such polarizations are rather easily induced. For poly (p-phenylene), however, how easily can such polarizations be induced? The energy required to polarize benzene to



is -2.683 γ, whereas the energy required to polarize planar biphenyl to



is -3.112 γ. (It should be recalled that γ is negative.) The difference is -0.429 γ. The extra resonance stabilization energy of biphenyl over benzene is, however, only +0.117 γ. Thus, if it is true that poly (p-phenylene) is planar because of the high resonance energy stablization, poly (p-phenylene) should be extremely unreactive to photon or phonon induced polarization because of the very high polarization energy.

F. THERMODYNAMICS OF PLANARIZATION

1. INTRODUCTION

We now turn to the last of the objections against the use of poly (p-phenylene)'s for TFOS — the energies required to planarize poly (p-phenylene)'s are too great for their being used as TFOS switches. For convenience we can consider polarization to occur in two steps although they are actually simultaneous. First, the rings are distorted to permit the planarization. Second, the electrons which are localized in the individual benzene rings are now allowed to delocalize. The free energy change for the total process is, therefore,

$$\text{(III-4)} \qquad \Delta G(\text{planarization}) = (\Delta H_d + \Delta H_e) - T(\Delta S_d + \Delta S_e) \;,$$

where 'd' and 'e' designate 'distortion' and 'electronic', respectively.

Since planarization requires the input of energy and decoupling of ortho-groups (when ortho-group coupling is present) from the benzene rings,

$$\text{(III-5)} \qquad \Delta H_d > 0$$

and

$$\text{(III-6)} \qquad \Delta S_d < 0 \;.$$

Furthermore, the energy of a delocalized electron is <u>less</u> than that for a localized electron, and the entropy of a delocalized electron is <u>greater</u> than that for a localized electron. Thus, (III-7) $$\Delta H_e < 0 ,$$

and

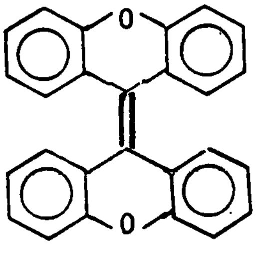
(III-8) $$\Delta S_e > 0 .$$

At the transition temperature $\Delta G = 0$, and

(III-9) $$T = \frac{\Delta H_d + \overline{\Delta H_e}}{\Delta S_e + \overline{\Delta S_d}} ,$$

where the bar over a term indicates that the term is negative.

For bixanthylene, for which the planar configuration is the 'lower' temperature form, ΔH_d and $\overline{\Delta H_e}$ have been estimated to be 20 kcal·mole^{-1} and −23 kcal·mole^{-1}, respectively [9]. The values of ΔS_e and $\overline{\Delta H_e}$ are strong functions of the amount of inter-ring coupling in the poly (p-phenylene)'s. It is important, therefore, that we have an independent means of estimating the amount of coupling. Fortunately, the optically active biphenyls provide such a means.



BIXANTHYLENE

2. ESTIMATION OF $\Delta S^{\ddagger}$ FOR OPTICALLY ACTIVE BIPHENYLS

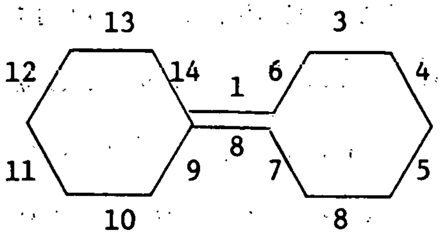
An optically active molecule is conceptually not superimposable with its mirror image. When an optically active biphenyl molecule planarizes, the two optically active configurations are equally probable as the form assumed when the molecule de-planarizes. Eventually, therefore, a solution of an optically active biphenyl contains equal numbers of the two configurations. The solution is now no longer optically active. This phenomenon is called 'racemization.'

The rates of racemization have been measured for several biphenyls. From the temperature dependence of the rate constant the entropy of activation, $\Delta S^{\ddagger}$, can be calculated. Since the 'transition state' of the racemization is the planar state,

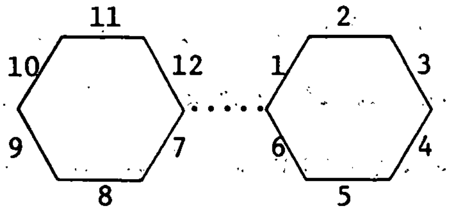
$$\Delta S^{\ddagger} = \Delta S_e + \overline{\Delta S_d} \, . \tag{III-10}$$

Thus, we can check the validity of our model for calculating $\Delta S_e + \overline{\Delta S_d}$ by comparing the calculated value with the experimental value. Values of $\Delta S^{\ddagger}$ for several biphenyls have been tabulated by Hall and Harris [56].

We have studied two models which we have called the 'strong coupling model' and the 'weak coupling model'. In the strong coupling model we assume that in the planar state the π-electrons are distributed in a closed loop of 14 parts. In the weak coupling model we assume two closed loops of 6 parts each. In the perpendicular state for both models each benzene ring consists of six parts.

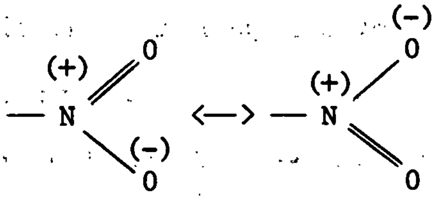


STRONG COUPLING MODEL

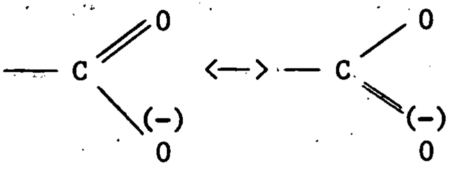


WEAK COUPLING MODEL

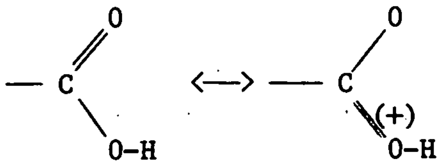
The nitro, carboxylate and carboxylic acid groups are assumed to have two interacting electrons, three parts when interacting with the benzene rings (when the benzene rings are <u>not</u> co-planar) and two parts when not interacting with the benzene rings (when the benzene rings are co-planar).



NITRO GROUP



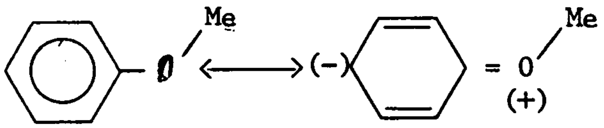
CARBOXYLATE GROUP



CARBOXYLIC ACID GROUP

The 'two parts' are the nitrogen - (or carbon -) oxygen bonds. The 'third part' is the nitrogen- (or carbon-) ring carbon bond.

For the methoxy group ($-OCH_3$ or $-OMe$) we assume one interacting electron and one part whether interacting with the ring or not interacting with the ring. The diagram below shows why a one electron interaction is assumed here.



The various entropy terms are calculated by

(III-11) $S = nR \ln p$,

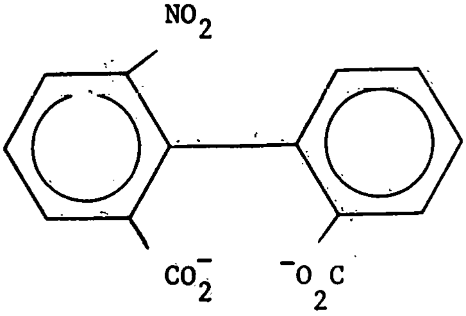
where

(III-12) n = number of electrons ,

(III-13) $R = 1.987 \text{ cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$,

and

(III-14) p = number of parts .



CASE I

For Case I for the strong coupling model the entropy for the coplanar state is

$$\text{(III-15)} \qquad S(\text{I}, \parallel, \text{strong}) = S(\phi\text{–}\phi) + 2S(-CO_2^-) + S(-NO_2)$$

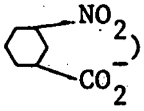
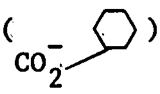
$$= 12R \ln 14 + 2(2R \ln 2) + 2R \ln 2$$

$$= 71.2 \ ,$$

and for the weak coupling model

$$\text{(III-16)} \qquad S(\text{I}, \parallel, \text{weak}) = 12 R \ln 12 + 3(2R \ln 2)$$

$$= 67.6 \ .$$

(III-17) $S(\text{I}, \perp) = S($  $) + S($  $)$

$$= 10R \ln 12 + 8R \ln 9$$

$$= 84.3 \ .$$

Thus, the values of $\Delta S = S(\parallel) - S(\perp)$ are given by

(III-18) $\Delta S(\text{I, strong}) = 71.2 - 84.3$

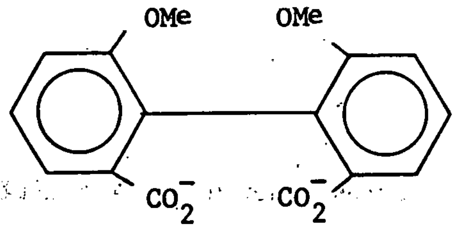
$$= -13.1 \text{ cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$$

and

(III-19) $\Delta S(\text{I, weak}) = 67.6 - 84.3$

$$= -16.7 \text{ cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1} .$$

The value reported by Hall and Harris is -11.2 $\text{cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$. For this case the strong coupling model gives the closer value.



CASE II

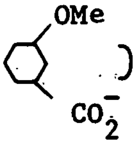
(III-20) $\Delta S(\text{II}, \|, \text{ strong}) = S(\phi\text{—}\phi) + 2S(-CO_2^-) + 2S(-OMe)$

$$= 12R \ln 14 + 2(2R \ln 2) + 2(R \ln 1)$$

$$= 68.4 ,$$

(III-21) $\Delta S(\text{II}, \|, \text{ weak}) = 12R \ln 12 + 4R \ln 2$

$$= 64.8 ,$$

(III-22) $S(\mathrm{II}, \perp) = 2S\Big($ 

$\Big)$

$$= 2(9R \ln 10)$$

$$= 82.4 \ ,$$

and

(III-23) $$\Delta S(\mathrm{II, strong}) = 68.4 - 82.4$$

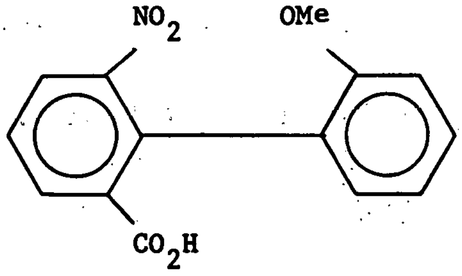
$$= -14.0 \ \mathrm{cal \cdot deg^{-1} \cdot mole^{-1}}$$

and

(III-24) $$\Delta S(\mathrm{II, weak}) = 64.8 - 82.4$$

$$= -17.6 \ \mathrm{cal \cdot deg^{-1} \cdot mole^{-1}} \ .$$

The observed value is -12.3 cal·deg^{-1}·mole^{-1}. Again the strong coupling model gives the closer value



CASE III

(III-25) $$S(\mathrm{III}, \parallel, \mathrm{strong}) = S(\phi\text{-}\phi) + S(-NO_2) + S(-CO_2H) + S(-OMe)$$

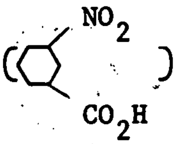
$$= 12R \ln 14 + 2R \ln 2 + 2R \ln 2 + R \ln 1$$

$$= 68.4 \ ,$$

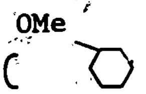
(III-26) $$S(\mathrm{III}, \parallel, \text{weak}) = 12R \ln 12 + 2R \ln 12 + 2R \ln 2 + R \ln 1$$

$$= 64.8 ,$$

(III-27) $S(\mathrm{III}, \perp) = S($



$) + S($



$)$

$$= 10R \ln 12 + 7R \ln 7$$

$$= 76.4 ,$$

and

(III-28) $$\Delta S(\mathrm{III}, \text{strong}) = 68.4 - 76.4$$

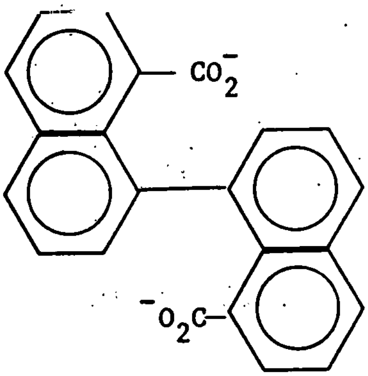
$$= -8.0 \text{ cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$$

and

(III-29) $$\Delta S(\mathrm{III}, \text{weak}) = 64.8 - 76.4$$

$$= -11.6 \text{ cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$$

The observed value is -7.3 cal$\cdot$deg$^{-1}\cdot$mole^{-1}. Once again the strong coupling model gives the better value. For our final example we will consider a binaphthyl. The strong coupling model requires 22 parts for the co-planar case. The weak coupling model requires 20 parts for the co-planar case.



CASE IV

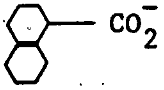
(III-30) $S(\text{IV}, \parallel, \text{strong}) = S(\text{binaphthyl}) + 2S(-CO_2^-)$

$= 20R \ln 22 + 2(2R \ln 2)$

$= 128.3$,

(III-31) $S(\text{IV}, \parallel, \text{weak}) = 20R \ln 20 + 4R \ln 2$

$= 124.6$,

(III-32) $S(\text{IV}, \perp) = 2S($  $)$

$= 2(12R \ln 13)$

$= 122.3$,

and

(III-33) $\Delta S(\text{IV}, \text{strong}) = 128.3 - 122.3$

$= +6.0\ \text{cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$,

and

(III-34) $\Delta S(\text{IV, weak}) = 124.6 - 122.3$

$= +2.3\ \text{cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$.

Hall and Harris report +9.2 $\text{cal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$. In each of the four cases the strong coupling model gives the closer value. Furthermore, the experimental value in each case is algebraically greater than the values for either model. Thus, the inter-ring coupling is actually greater than that of the strong coupling model.

3. ΔS FOR POLY (p-PHENYLENE)

Let q be the number of benzene rings, each of which supplies six electrons. In the strong coupling model the first ring in the fully planar state supplies six parts. The subsequent rings supply eight parts each. Thus,

(III-35) number of electrons, planar state $= 6q$,

(III-36) number of parts, planar state $= 6 + 8(q-1)$

$= 8q-2$,

and, by (III-11),

$$S(\parallel) = 6qR \ln(8q-2) \,, \tag{III-37}$$

$$\begin{aligned} S(\perp) &= q(6R \ln 6) \\ &= 6qR \ln 6 \,, \end{aligned} \tag{III-38}$$

and

$$\begin{aligned} \Delta S_e &= 6qR \ln\left(\frac{8q-2}{6}\right) \\ &= 6qR \ln\left(\frac{4q-1}{3}\right) . \end{aligned} \tag{III-39}$$

For poly (p-phenylene) itself $\Delta S_d = 0$ since the hydrogens are not coupled to the rings by π-linages.

4. ΔH FOR POLY (p-PHENYLENE)

The energy of the j-th energy level for the one dimensional FE-MO (Free Electron-Molecular Orbital) model is given by [57]

$$E_j = K\left(\frac{n_j}{p}\right)^2 \,, \tag{III-40}$$

where K is a constant, n_j is the quantum number of the energy level and p is the number of parts given by (III-36). Since two electrons occupy each energy level,

(III-41)
$$E_{TOTAL} = \frac{K}{p^2} \sum_{j=1}^{6q} n_j^2$$
$$= \frac{2K}{(8q-2)^2} \sum_{j=1}^{3q} j^2$$
$$= \frac{K}{2(4q-1)^2} \sum_{j=1}^{3q} j^2 .$$

Since

(III-42)
$$\sum_{j=1}^{n} j^2 = \frac{n(n+1)(2n+1)}{6} ,$$

we may write (III-41) as

(III-43)
$$E_{TOTAL} = \frac{K}{2(4q-1)^2} \cdot \frac{3q(3q+1)(6q+1)}{6}$$
$$= \frac{K}{4} \cdot \frac{q(3q+1)(6q+1)}{(4q-1)^2}$$

For benzene, q = 1. Thus

(III-44)
$$E_{TOTAL}(\text{BENZENE}) = \frac{K}{4} \cdot \frac{4(7)}{9}$$
$$= \frac{7K}{9} .$$

For biphenyl, q = 2. Thus,

(III-45)
$$E_{TOTAL}(\text{BIPHENYL}) = \frac{K}{4} \cdot \frac{2(7)(13)}{7(7)}$$
$$= \frac{13K}{14}$$

Since there is very little volume change in the solid on planarization, we may equate E and the enthalpy. Since biphenyl consists of two benzene rings,

(III-46) $$\Delta H_e(\text{BIPHENYL}) = E_{\text{TOTAL}}(\text{BIPHENYL}) - 2E_{\text{TOTAL}}(\text{BENZENE})$$

$$= \frac{13K}{14} - \frac{14K}{9}$$

$$= -0.627K.$$

In SECTION III.C we indicated that the 'excess' resonance energy of fluorene over twice benzene is 3.9 - 4.9 $\text{kcal}\cdot\text{mole}^{-1}$, where resonance energy is taken as a positive number. Thus, we now take

(III-47) $$\Delta H_e(\text{BIPHENYL}) = -4.4\ \text{kcal}\cdot\text{mole}^{-1},$$

and

(III-48) $$K = \frac{-4.4}{-0.627}$$

$$= 7.02 \times 10^3\ \text{cal}\cdot\text{mole}^{-1}.$$

For q mers there are q-1 inter-mer bonds. If ΔH_d is the value for one bond, then

$$
\begin{aligned}
\text{(III-49)}\qquad \Delta H &= (q-1)\ \Delta H_d + E_{TOTAL} - q\ E_{TOTAL}(\text{BENZENE}) \\
&= (q-1)\ \Delta H_d + \frac{K}{4}\,\frac{q(3q+1)(6q+1)}{(4q+1)^2} - \frac{7Kq}{9} \\
&= (q-1)\ \Delta H_d + 7.02 \times 10^3 \left[\frac{q(3q+1)(6q+1)}{4(4q-1)^2} - \frac{7q}{9}\right] .
\end{aligned}
$$

5. T (TRANSITION) FOR POLY (p-PHENYLENE)

We may now substitute (III-49) and (III-39) into (III-9) and obtain

$$
\text{(III-50)}\qquad T_{(\text{TRANSITION})} = \frac{(q-1)\ \Delta H_d + 7.02 \times 10^3\left[\frac{q(3q+1)(6q+1)}{4(4q-1)^2} - \frac{7q}{9}\right]}{6qR\ \ln\left(\frac{4q-1}{3}\right)} .
$$

If $q = 40$ and $\Delta H_d = 1.8 \times 10^4\ \text{cal}\cdot\text{mole}^{-1}$, then

$$
\text{(III-51)}\qquad T(q = 40,\ \Delta H_d = 1.8 \times 10^4) = 299°\text{K} .
$$

If $q = 100$ and $\Delta H_d = 1.8 \times 10^4\ \text{cal}\cdot\text{mole}^{-1}$, then

$$
\text{(III-52)}\qquad T(q = 100,\ \Delta H_d = 1.8 \times 10^4) = 246°\text{K} .
$$

Thus, we see that we can make a polymer which will switch at 25°C or a polymer which is switched on all of the time just by changing the polymer length.

In TABLE III-3 are listed the various data which have been obtained by the use of equation (III-50). The values which have been circumscribed with rectangles are those which are closest to the switching temperature of 298°K (25°C). The last row in the TABLE has the change in the switching temperature per unit change in the number of mers. Since it is most unlikely that a production process will produce a very narrow distribution of chain lengths, this number should be as small as possible.

The average value of $\Delta H^{\ddagger}$ for the biphenyls listed by Hall and Harris [56] is 22.2 kcal·mole^{-1}. Since this already inclues a $\overline{\Delta H_e}$ of about -4.4 kcal·mole^{-1}, it is estimated from their data that ΔH_d is 26-27 kcal·mole^{-1}. Since their ortho-substituents are larger than the ones which we would use, a value of H_d in (III-50) of 23-25 kcal·mole^{-1} is not unreasonable. It should be noted that the ΔH_d used in equation (III-50) is an averaged value. For practical reasons it may be desirable to have different values of ΔH_d for various inter-ring bonds.

For $\Delta H_d = 23$ kcal·mole^{-1} and $q = 187$ the transition temperature is 298.0°K. The temperature change per unit change in the number of mers is 0.28. If we assume a 15 mer spread in the chain lengths, the spread in the transition temperature would be 4.2 degrees.

The above analysis, while reasonable, is incomplete. There are factors which have not been taken into consideration. For example, the variations of bond lengths and angles which occur as a result of planarization effect the σ-bond energies as well as the π-bond energies. A more exact method for calculating the ΔH's and ΔS's is most desirable. As an aid to the attaining of this goal we have developed 'Equilibrium Bond Length' (EBL) theory.

TABLE III-3

TRANSITION TEMPERATURES(a)

q \ H_d(b)	15	16	17	18	19	20	21	22	23	24	25
2	524.6	574.1	623.6	673.1	722.6	772.1	821.6	871.1	920.6	970.1	1019.6
5	406.8	443.1	479.5	515.8	552.2	588.5	624.9	661.2	697.6	734.4	770.3
10	334.3	363.7	393.1	422.6	452.0	481.0	510.9	540.3	569.7	597.2	628.6
15	$\boxed{299.9}$	326.2	352.4	378.7	405.0	431.3	457.6	483.8	510.1	536.4	562.7
20	278.6	$\boxed{303.0}$	327.4	351.7	376.1	400.5	424.8	449.2	473.5	497.9	522.3
30	252.5	274.6	$\boxed{296.6}$	318.6	340.7	362.7	384.7	406.8	428.8	450.8	472.8
40	236.4	257.0	277.6	$\boxed{298.2}$	318.8	339.4	360.0	380.6	401.2	421.8	442.4
50	225.0	244.6	264.2	283.8	$\boxed{303.4}$	323.0	342.6	362.2	381.8	401.4	421.0
60	216.5	235.3	254.1	273.0	291.8	310.7	329.5	348.3	367.2	386.0	404.9
70	209.6	227.9	246.1	264.4	282.6	$\boxed{300.8}$	319.1	337.3	355.6	373.8	392.1
80	204.0	221.8	239.5	257.3	275.0	292.8	310.5	328.3	346.0	363.8	381.5
90	199.3	216.7	234.0	251.3	268.7	286.0	303.3	320.7	338.0	355.3	372.7
100	195.3	212.2	229.2	246.2	263.2	280.2	$\boxed{297.1}$	314.1	331.1	348.1	365.1
110	191.7	208.4	225.1	241.7	258.4	275.1	291.7	308.4	325.1	341.8	358.4
120	188.6	205.0	221.4	237.8	254.2	270.6	287.0	303.4	319.8	336.2	352.5
130	185.8	201.9	218.1	234.2	250.2	266.5	282.7	$\boxed{298.8}$	314.0	331.1	347.3
140	183.3	199.2	215.1	231.1	247.0	262.9	278.8	294.8	310.7	326.6	342.6
150	181.0	196.7	212.4	228.2	243.9	259.6	275.4	291.1	306.8	322.5	338.3
160	178.9	194.4	210.0	225.5	241.1	256.6	272.2	287.7	303.3	318.8	334.3
170	176.9	192.3	207.7	223.1	238.5	253.8	269.2	284.6	300.0	315.4	330.7
180	175.2	190.4	205.6	220.8	236.1	251.3	266.5	281.7	$\boxed{296.9}$	312.2	327.4
190	173.5	188.6	203.7	218.7	233.8	248.9	264.0	279.1	294.1	309.2	324.3
200	172.0	186.9	201.8	216.8	231.7	246.7	261.6	276.6	291.5	306.5	321.4
250										$\boxed{295.0}$	
290										287.8	301.8
300											300.2
310											$\boxed{298.6}$
320											297.0
Deg/ Mer	5.6	4.5	2.5	1.7	1.4	0.90	0.58	0.43	0.32	0.21	0.16

(a) Degrees Kelvin (b) Kcal·mole^{-1}

IV. EQUILIBRIUM BOND LENGTH THEORY

A. INTRODUCTION

In addition to our need to have a more exact theoretical understanding of the poly (p-phenylenes) recent advances in the synthesis of thin films of polyacetylene have brought up again the question of the values of the various bond lengths in MCMM such as the polyenes [58]. As the length of the polymer molecule is increased, do the carbon-carbon bond lengths tend to 'even out', or does the alternating bond length pattern of small molecules such as butadiene continue? Ab initio calculations for such large molecules are prohibitively expensive. It is, therefore, desirable to develop an approximation method which can be used to address this question.

One of the simplest cases of the application of Schrödinger's equation to solve is the 'particle in a box'. [In SECTION III we referred to the particle in a box problem as the FE-MO method. Although the latter name is the one used most frequently, the former name is more accurate since it is assumed that there are no Coulombic interactions among the particles.] Here it is assumed that the potential energy is uniformly zero inside the box and positively infinite everywhere outside of the box. If the box is a rectangular parallelopiped, the solutions for the kinetic energy of the particle are given by

$$\text{(IV-1)} \qquad E(\text{kinetic}) = \frac{h^2}{8m}\left[\left(\frac{n_1}{a_1}\right)^2 + \left(\frac{n_2}{a_2}\right)^2 + \left(\frac{n_3}{a_3}\right)^2\right],$$

where h is Planck's constant, m is the rest mass of the particle, a_j is the Cartesian coordinate dimension of the box for the j-th coordinate, and n_j is the quantum number associated with the j-th coordinate.

If each of the a_j's is reduced by a factor of two, the kinetic energy of the particle is increased by a factor of four. In anthropomorphic terms the particle becomes more agitated as the size of the room decreases. The particle may, therefore, be considered to have claustrophobia, and the energy of equation (IV-1) may be considered to be the 'claustrophobic energy'. From the viewpoint of the mathematics or the physics such picturesque terminology is unnecessary, but it does have considerable didactic utility.

From the viewpoint of Coulomb's equation,

$$V = (4\pi\varepsilon_o)^{-1} \sum_i \sum_{j>i} q_i q_j / r_{ij} \,, \tag{IV-2}$$

where ε_o is the permittivity of vacuum, q_i is the charge on the i-th particle, q_j is the charge on the j-th particle, and r_{ij} is the distance between the centers of charge, many systems of 'point' charges should collapse to a single point. Why such a catastrophe does not occur in the hydrogen atom was one of the difficult questions facing the founders of quantum mechanics. The claustrophobic energy answer is that, although the potential energy decreases as r_{ij} approaches zero, the claustrophobic energy increases. The equilibrium value of r_{ij} is that for which the total energy of the system is minimized.

Since the kinetic energy cannot be zero, the system will oscillate about the equilibrium value of r_{ij}.

B. THE HYDROGEN ATOM

At least three different radii can be defined for the hydrogen atom

(IV-3) $$\langle r\rangle = \int u^* r u d\tau ,$$

(IV-4) $$\sqrt{\langle r^2\rangle} = [\int u^* r^2 u d\tau]^{1/2} ,$$

and the 'most probable value' which is obtained by the solution of

(IV-5) $$\frac{dP(r)}{dr} = 0 ,$$

where $P(r)$ is the radial probability distribution function for the hydrogen atom [59].

The radial wave functions for the first three s-orbitals of hydrogen are

(IV-6) $$R_{1,0} = 2(a_o)^{-3/2} e^{-\rho} ,$$

(IV-7) $$R_{2,0} = (2)^{-3/2} (a_o)^{-3/2} (2-\rho) e^{-\rho/2} ,$$

and

(IV-8) $$R_{3,0} = 2(3)^{-9/2} (a_o)^{-3/2} (27 - 18\rho + 2\rho^2) e^{-\rho/3} ,$$

where

(IV-9) $$\rho = r/a_0$$

and

(IV-10) $$a_o = \frac{\varepsilon_o h^2}{\pi m_o \; e_o^2} ,$$

where m_o and e_o are the rest mass and the magnitude of the charge of the electron, respectively. a_o is the 'Bohr radius'. The relationship between $P(r)$ and $R_{n,\ell}$ is given by

(IV-11) $$P(r)dr = [R_{n,\ell}(r)]^2 \; r^2 \; dr \quad .$$

For $n = 1$,

(IV-12) $$\begin{aligned} \langle r \rangle &= \frac{4}{a_o^3} \int_0^\infty e^{-2\rho} \; r^3 \; dr \\ &= \frac{4}{a_o^3} \int_0^\infty e^{-2\beta} (a_o \rho)^3 \; d(a_o \rho) \\ &= 4a_o \int_0^\infty e^{-2\rho} \; \rho^3 \; d\rho \\ &= 4a_o \left[\frac{-e^{-2}}{(2)^4} \{ (2\rho)^3 + 3(2\rho)^2 + 6(2\rho) + 6 \} \right]_0^\infty \\ &= 4a_o [\tfrac{6}{16}] \\ &= 3a_o/2 \; , \end{aligned}$$

(IV-13) $$\sqrt{\langle r^2\rangle} = \left[\frac{4}{a_o^3} \int_0^\infty e^{-2\rho}\, r^4\, dr\right]^{1/2}$$

$$= \left[4a_o^2 \int_0^\infty e^{-2\rho}\, \rho^4\, d\rho\right]^{1/2}$$

$$= \left\{4a_o^2\left[\frac{-e^{-2\rho}}{(2)^5} \{(2\rho)^4 + 4(2\rho)^3 + 12(2\rho)^2 + 24(2\rho) + 24\}\right]_0^\infty\right\}^{1/2}$$

$$= \left\{4a_o^2\left(\frac{24}{32}\right)\right\}^{1/2}$$

$$= \sqrt{3}\ a_o\ ,$$

and

$$\frac{dP(r)}{dr} = \frac{4}{a_o^3}\ \left(2r\ e^{-2r/ao} - \frac{2}{a_o}\, r^2\ e^{-2r/ao}\right)$$

$$= 0\ ,$$

$$2r = \frac{2r^2}{a_o}\ ,$$

or

(IV-14) $$r(\text{most probable}) = a_o\ .$$

For n = 2,

(IV-15)
$$\langle r\rangle = \frac{1}{8a_o^3}\int_0^\infty (2-\rho)^2\, e^{-\rho}\, r^3\, dr$$

$$= \frac{a_o}{8}\int_0^\infty (4-4\rho+\rho^2)\ \rho^3\ e^{-\rho}\ d\rho$$

$$= \frac{a_o}{8}\int_0^\infty (4\rho^3-4\rho^4+\rho^5)\ e^{-\rho}\ d\rho$$

$$= \frac{a_o}{8}\Bigg[4\Big\{\frac{-e^{-\rho}}{(1)^4}\Big\{\rho^3 + 3\rho^2 + 6\rho + 6\Big\}\Big\}$$

$$- 4\Big\{\frac{-e^{-\rho}}{(1)^5}\Big\{\rho^4 + 4\rho^3 + 12\rho^2 + 24\rho + 24\Big\}\Big\}$$

$$+ \Big\{\frac{-e^{-\rho}}{(1)^6}\Big\{\rho^5 + 5\rho^4 + 20\rho^3 + 60\rho^2 + 120 + 120\Big\}\Big\}\Bigg]_0^\infty$$

$$= \frac{a_o}{8}\,[24 - 96 + 120]$$

$$= 6a_o\ ,$$

(IV-16)
$$\sqrt{\langle r^2\rangle} = \left[\frac{1}{8a_o^3}\int_0^\infty (2-\rho)^2\ e^{-\rho}\ r^4\ dr\right]^{1/2}$$

$$= \left[\frac{a_o^2}{8}\int_0^\infty (4\rho^4 - 4\rho^5 + \rho^6)\ e^{-\rho}\ d\rho\right]^{1/2}$$

$$= \Bigg\{\frac{a_o^2}{8}\Big[4\{-e^{-\rho}(\rho^4 + 4\rho^3 + 12\rho^2 + 24\rho + 24)\}$$

$$-4\{-e^{-\rho}(\rho^5 + 5\rho^4 + 20\rho^3 + 60\rho^2 + 120\rho + 120)\}$$

$$+ \{-e^{-\rho}(\rho^6 + 6\rho^5 + 30\rho^4 + 120\rho^3 + 360\rho^2 + 720\rho + 720)\}\Big]_0^\infty\Bigg\}^{1/2}$$

$$= \left\{\frac{a_o^2}{8}\,(96 - 480 + 720)\right\}^{1/2}$$

$$= \sqrt{42}\ a_o\ ,$$

and

$$\frac{dP(r)}{dr} = \frac{1}{8a_o^3}\left[\frac{-2}{a_o}\left(2 - \frac{r}{a_o}\right) e^{-r/a_o} r^2 + \left(2 - \frac{r}{a_o}\right)^2 \left(- \frac{1}{a_o}\right) e^{-r/a_o} r^2 - 2r\left(2 - \frac{r}{a_o}\right)^2 e^{-r/a_o}\right]$$

$$= 0 ,$$

$$\frac{2\left(2 - \frac{r}{a_o}\right) r^2}{a_o} + \frac{\left(2 - \frac{r}{a_o}\right)^2 r^2}{a_o} = 2r\left(2 - \frac{r}{a_o}\right)^2 ,$$

$$\frac{2r^2}{a_o} + \frac{\left(2 - \frac{r}{a_o}\right) r^2}{a_o} = 2r\left(2 - \frac{r}{a_o}\right)$$

$$2r^2 a_o + (2a_o - r) r^2 = 2r(2a_o^2 - a_o r) ,$$

$$2a_o r^2 + 2a_o r^2 - r^3 = 4a_o^2 r - 2a_o r^2 ,$$

$$r^3 - 6a_o r^2 + 4a_o^2 r = 0 ,$$

$$r = 0, \quad r^2 - 6a_o r + 4a^2 = 0 ,$$

$$r = \frac{6a \pm \sqrt{36a_o^2 - 16a^2}}{2}$$

$$= 3a_o \pm \sqrt{5}\, a_o ,$$

or

(IV-17) $$r(\text{most probable}) = 0, \quad (3 - \sqrt{5})\, a_o, \quad (3 + \sqrt{5})\, a_o \,.$$

For n = 3,

(IV-18) $$\langle r \rangle = \frac{4}{19{,}683\, a_o^3} \int_0^\infty (729 - 972\rho + 432\rho^2 - 72\rho^3 + 4\rho^4)\, e^{-2\rho/3}\, r^3 dr$$

$$= \frac{4a_o}{19683} \int_0^\infty (729\rho^3 - 972\rho^4 + 432\rho^5 - 72\rho^6 + 4\rho^7)\, e^{-2\rho/3}\, d\rho$$

$$= \frac{4a_o}{19{,}683} \Big[729(\tfrac{3}{2})^4\, (3!) - 972(\tfrac{3}{2})^5\, (4!) + 432(\tfrac{3}{2})^6\, (5!)$$

$$-72(\tfrac{3}{2})^7\, (6!) + 4(\tfrac{3}{2})^8\, (7!) \Big]$$

$$= \frac{4a_o}{19{,}683}\, [66{,}430.125]$$

$$= 13.5\, a_o \,,$$

(IV-19) $$\sqrt{\langle r^2 \rangle} = \left[\frac{4a_o^2}{19{,}683} \int_0^\infty (729\rho^4 - 972\rho^5 + 432\rho^6 - 72\rho^7 + 4\rho^8)\, e^{-2\rho/3}\, d\rho \right]^{1/2}$$

$$= \Big[\frac{4a_o^2}{19{,}683} \{ 729(\tfrac{3}{2})^5\, (4!) - 972(\tfrac{3}{2})^6\, (5!) + 432(\tfrac{3}{2})^7\, (6!)$$

$$- 72(\tfrac{3}{2})^8\, (7!) + 4(\tfrac{3}{2})^8\, (8!) \} \Big]^{1/2}$$

$$= \left[\frac{4a_o^2}{19{,}683}\, (1{,}018{,}595.25) \right]^{1/2}$$

$$= [207\, a_o^2]^{1/2}$$

$$= \sqrt{207}\, a_o \,,$$

and

$$\frac{dP(r)}{d} = \frac{4}{19{,}683\ a_o^2}\Big[2(27\rho - 18\rho^2 + 2\rho^3)\ (27 - 36\rho + 6\rho^2)\ e^{-2\rho/3}$$

$$+ (27\rho - 18\rho^2 + 2\rho^3)^2\ (\tfrac{-2}{3})\ e^{-2\rho/3}\Big]$$

$$= 0\ ,$$

$$2(27\rho - 18\rho^2 + 2\rho^3)\ (27 - 36\rho + 6\rho^2) - \frac{2}{3}\,(27\rho - 18\rho^2 + 2\rho^3)^2 = 0\ ,$$

$$2(27 - 36\rho + 6\rho^2) - \frac{2}{3}\,(27\rho - 18\rho^2 + 2\rho^3) = 0\ ,$$

$$27 - 36\rho + 6\rho^2 - 9\rho + 6\rho^2 - \frac{2}{3}\,\rho^3 = 0\ ,$$

$$-\frac{2}{3}\,\rho^3 + 12\rho^2 - 45\rho + 27 = 0\ ,$$

or

$$2\rho^3 - 36\rho^2 + 135\rho - 81 = 0\ ,$$

and from

$$27\rho - 18\rho^2 + 2\rho^3 = 0$$

$$\rho = 0,\quad 2\rho^2 - 18\rho + 27 = 0\ .$$

The roots of these equations are

(IV-20) $$\rho = 13.074\ ,\qquad r = 13.074\ a_o$$

$$\rho = 4.186\ ,\qquad r = 4.186\ a_o$$

$$\rho = 0.740\ ,\qquad r = 0.740\ a_o\ ,$$

(IV-21) $$\rho = 0\ , \qquad r = 0$$

and

(IV-22) $$\rho = \frac{18 \pm \sqrt{324 - 216}}{4} = \frac{18 \pm \sqrt{108}}{4}$$

$$r = \frac{9 \pm \sqrt{27}}{2}\, a_o\ .$$

The results of these calculations are summarized in TABLE IV-1. It is to be noted that the values of $\langle r \rangle$ are in the ratio $1:4:9 = 1^2:2^2:3^2$.

The correct geometry to use for the kinetic energy term for the hydrogen atom is, of course, the sphere. We shall, however, restrict our present discussion to equation (IV-1) as written. We shall treat the one dimensional case and the three dimensional case. It should be noted that a_j is effectively a diameter and not a radius. We shall, therefore, take $a_j = fr$, where the value of f is to be determined.

For the one dimensional case,

(IV-23) $$E(\text{total}) = \frac{h^2 n^2}{8 m_o f^2 r^2} - \frac{e_o^2}{4\pi\varepsilon_o r}\ ,$$

$$\frac{dE(\text{total})}{dr} = \frac{-2h^2 n^2}{8 m_o f^2 r^2} + \frac{e_o^2}{4\pi\varepsilon_o r^2}$$

$$= 0\ ,$$

TABLE IV-1

RADIUS VALUES FOR HYDROGEN s-ORBITALS

(in units of a_0)

n	$\langle r \rangle$	$\sqrt{\langle r^2 \rangle}$	r (most probable)
1	1.500	1.732	1.000
2	6.000	6.481	5.236
			0.764
			0.000
3	13.500	14.387	13.074
			7.098
			4.186
			1.902
			0.740
			0.000

(IV-24)
$$r = \frac{\pi h^2 \varepsilon_o}{m_o e_o^2} \cdot \frac{n^2}{f^2}$$

$$= \frac{\pi^2 a_o n^2}{f^2} \qquad \text{[by (IV-10)]} .$$

Since this r is proportional to n^2, we assume that it is $\langle r \rangle$. Thus, for $n = 1$

$$1.5\, a_o = \frac{\pi^2 a_o}{f^2} \quad ,$$

$$f^2 = \pi^2/1.5$$

and

(IV-25)
$$f = 2.565 .$$

The Van der Waals radius of hydrogen is 1.2Å [60]. In Bohr radii this value is 2.268 B·r. The ratio between this value and $\langle r \rangle$ is 1.512. Since f is a diameter factor rather than a radius factor,

(IV-26)
$$f(\text{experimental}) = 2(1.512)$$

$$= 3.024 .$$

For the three dimensional model with $n_1 = n_2 = n_3 = 1$, and $a_1 = a_2 = a_3 = fr$, we have

(IV-27) $$E(\text{total}) = \frac{3h^2}{8m_o f^2 r^2} - \frac{e_o^2}{4\pi\varepsilon_o r} ,$$

$$\frac{dE(\text{total})}{dr} = \frac{-3h^2}{4m_o f^2 r^2} + \frac{e_o^2}{4\pi\varepsilon_o r^2}$$

$$= 0 ,$$

(IV-28) $$r = \frac{3\pi^2 a_o}{f^2} ,$$

and

(IV-29) $$f = [3\pi^2/1.5]^{1/2}$$

$$= 4.443 .$$

Since the Van der Waal diameter would correspond to the body diagonal of the cube, but a is the edge dimension, we must divide f by $\sqrt{3}$. Thus,

(IV-30) $$f' = \frac{f}{\sqrt{3}}$$

$$= 2.565 ,$$

which is exactly the same as the one dimensional, model value. This value is 15% less than the 'experimental' value. When one considers the crudeness of the model used here, this degree of agreement is fortuitous or fantastic!

C. THE HYDROGEN MOLECULE ION

For the hydrogen molecule ion we shall take r_+ as the distance between the protons. We shall assume that the electron is on the plane midway between the protons and perpendicular to the line of centers. The perpendicular distance from the electron to the line of centers is $r_-/2$. Thus, the distance between a proton and the electron is

$$d = \frac{1}{2}\,(r_+^2 + r_-^2)^{1/2} \,, \tag{IV-31}$$

and

$$E(\text{total}) = \frac{h^2}{8m_o f^2}\left(\frac{1}{r_+^2} + \frac{2}{r_-^2}\right) - \frac{e_o^2}{4\pi\varepsilon_o}\left(\frac{4}{\sqrt{r_+^2+r_-^2}} - \frac{1}{r_+}\right) \,, \tag{IV-32}$$

where the factor of 2 in the kinetic energy term is the result of our taking <u>two</u> Cartesian coordinate axes perpendicular to the line of centers coordinate axis. We now divide (IV-32) by $e_o^2/4\pi\varepsilon_o$ to obtain

$$E(\text{total})\left\{4\pi\varepsilon_o/e_o^2\right\} \tag{IV-33}$$

$$= \frac{\pi^2 a_o}{2f^2}\left(\frac{1}{r_+^2} + \frac{1}{r_-^2}\right) - \frac{4}{\sqrt{r_+^2+r_-^2}} + \frac{1}{r_+}$$

$$= \frac{\pi^2(5.2918 \times 10^{-11})}{2f^2}\left(\frac{1}{r_+^2} + \frac{2}{r_-^2}\right) - \frac{4}{\sqrt{r_+^2+r_-^2}} + \frac{1}{r_+}$$

$$= \frac{2.6114 \times 10^{-10}}{f^2}\left(\frac{1}{r_+^2} + \frac{2}{r_-^2}\right) - \frac{4}{\sqrt{r_+^2+r_-^2}} + \frac{1}{r_+} \,.$$

If we now take r_+ and r_- in Å units instead of in meters,

$$\text{(IV-34)} \qquad \frac{4\pi\varepsilon_o \times 10^{-10}}{e_o^2} E(\text{total})$$

$$= \frac{2.6114}{f^2}\left(\frac{1}{r_+^2} + \frac{2}{r_-^2}\right) - \frac{4}{\sqrt{r_+^2+r_-^2}} + \frac{1}{r_+} .$$

We shall now minimize the left hand side of (IV-34) for a given value of f by varying the values of r_+ and r_-. The results of this analysis are given in TABLE IV-2. The experimental value for the equilibrium bond length for the hydrogen molecule ion is 1.06×10^{-10} meters [61]. If 3.024 is taken as the correct value for f, the value 2.913 is 3.7% to low, a remarkably good correspondence.

D. THE HYDROGEN MOLECULE

We shall assume that the electron added to the hydrogen molecule ion to form the hydrogen molecule is on the other side of the line of centers of the protons from the first electron but at the same distance from the line of centers. This doubles the kinetic energy term and the attraction potential energy term. It also adds a new repulsion energy term. Thus, (IV-34) becomes

$$\text{(IV-35)} \qquad \frac{4\pi\varepsilon_o \times 10^{-10}}{e_o^2} E(\text{total})$$

$$= \frac{5.228}{f^2}\left(\frac{1}{r_+^2} + \frac{2}{r_-^2}\right) - \frac{8}{\sqrt{r_+^2+r_-^2}} + \frac{1}{r_+} + \frac{1}{r_-} .$$

TABLE IV-2

Equilibrium Bond Length of H_2^+ as a Function of f

f	$r_+ \times 10^{10}$ meters	$r_- \times 10^{10}$ meters
3.628	0.685	0.634
3.500	0.734	0.680
3.400	0.778	0.720
3.200	0.877	0.812
3.000	0.999	0.924
2.950	1.034	0.957
2.913	1.060	0.981

TABLE IV-3

Equilibrium Bond Length of H_2 as a Function of f

f	$r_+ \times 10^{10}$ meters	$r_- \times 10^{10}$ meters
2.913	0.925	1.045
3.000	0.873	0.987
3.223	0.755	0.853
3.251	0.742	0.838
3.255	0.740	0.836

The results of this analysis are listed in TABLE IV-3. The experimental value of the equilibrium bond length for the hydrogen molecule is 0.74×10^{-10} meters [62]. If again 3.024 is taken as the correct value for f, the value 3.255 is 7.6% too high. Again we have a remarkably good correspondence. Since our primary interest in this study is <u>not</u> diatomic molecules, we shall not purse this subject further here. Instead, we shall proceed to the analysis of polyenes.

E. MOLECULAR ORBITAL THEORY

The APPENDIX to this report, 'Molecular Quantum Mechanics' is essentially SECTION III of TFOS-B. Two equations which we shall use extensively here are

$$E_k = \alpha - \frac{\gamma\lambda_k}{1 - \$\lambda_k} \tag{A-48}$$

in which E_k is the energy of the k-th molecular orbital, α, $\$$ and λ are the Coulombic integral, adjacent overlap integral and modified adjacent exchange integral for $2p_\pi$-orbitals in benzene, and λ_k is the quantum number for the k-th molecular orbital, and

$$(-\rho_{ji})|\bar{Z}_{ik}\rangle = \lambda_k|\bar{Z}_{ik}\rangle \tag{A-52}$$

or

$$(\lambda_k\, \delta_{ji} + \rho_{ji})|\bar{Z}_{ik}\rangle \tag{IV-36}$$

in which δ_{ji} is the Kronecker delta $[\delta_{ji} = 1.00$ for $j = i$ and $\delta_{ji} = 0.00$ for $j \neq i]$, $|\bar{Z}_{ik}\rangle$ is the eigenvector for the k-th molecular orbital and

(IV-37) $$\rho_{ji} = \frac{\$_{ji}(1 - \delta_{ji})}{\$} ,$$

where $\$_{ji}$ is the overlap integral for the j-th and i-th atomic orbitals. If both of the atomic orbitals are carbon $2p_\pi$-orbitals, $\$_{ji}$ is given by (A-140) and (A-141).

The $\$_{ji}$ integrals were evaluated using Slater orbitals for the carbon $2p_\pi$-orbitals, taken as $2p_y$-orbitals,

(IV-38) $$u(2p_y) = 1.899y\ e^{-1.625r'} ,$$

where r' is the distance between the atoms in Bohr radii (0.529×10^{-10} meters) [63, 64, 65]. The results of these calculations are summarized in TABLE IV-4, which is TABLE A-1 in terms of r rather than a (meters rather than Bohr radii).

The relation between r and \$ is not quite linear. Within the accuracy of the methodology used here, however, the error introduced by assuming linearity is not serious. If the function were linear,

(IV-39) $$\frac{\Delta\$}{-\Delta r} = \frac{0.3454 - 0.1902}{(1.545 - 1.185) \times 10^{-10}}$$
$$= 4.311 \times 10^{9} .$$

If this value is used with the equation,

(IV-40) $$\$_j = \$_o + \frac{\Delta\$}{-\Delta r}(r_o - r_j) ,$$

TABLE IV-4

Carbon-Carbon $2p_y$-$2p_y$ Overlap Integrals as a Function of the Interatomic Distance

r × 10^{10} meters	$	r × 10^{10} meters	$	r × 10^{10} meters	$
1.185	0.3454	1.307	0.2849	1.428	0.2327
1.190	0.3425	1.312	0.2824	1.434	0.2306
1.196	0.3398	1.317	0.2800	1.439	0.2285
1.201	0.3370	1.322	0.2776	1.444	0.2265
1.206	0.3342	1.328	0.2752	1.449	0.2245
1.211	0.3315	1.333	0.2728	1.455	0.2224
1.217	0.3288	1.338	0.2705	1.460	0.2204
1.222	0.3261	1.344	0.2681	1.465	0.2184
1.227	0.3234	1.349	0.2658	1.471	0.2164
1.233	0.3207	1.354	0.2635	1.476	0.2145
1.238	0.3180	1.360	0.2612	1.481	0.2125
1.243	0.3154	1.365	0.2589	1.486	0.2106
1.248	0.3127	1.370	0.2566	1.492	0.2087
1.254	0.3101	1.375	0.2544	1.497	0.2067
1.259	0.3075	1.381	0.2521	1.502	0.2048
1.264	0.3050	1.386	0.2499	1.508	0.2030
1.270	0.3024	1.391	0.2477	1.513	0.2011
1.275	0.2998	1.397	0.2455	1.518	0.1992
1.280	0.2973	1.402	0.2434	1.524	0.1974
1.285	0.2948	1.407	0.2412	1.529	0.1956
1.291	0.2923	1.412	0.2390	1.534	0.1938
1.296	0.2898	1.418	0.2369	1.539	0.1920
1.301	0.2873	1.423	0.2348	1.545	0.1902

with $r_o = 1.365 \times 10^{-10}$ and $\$_o = 0.2589$, the errors in the calculated values of $\$$ for $r = 1.185 \times 10^{-10}$ and $r = 1.545 \times 10^{-10}$ are 2.58% and 4.68%, respectively. A better 'end points' fit is obtained if the slope is taken as -4.168×10^9. In this case (IV-40) becomes

$$\text{(IV-41)} \qquad \$_j = 0.2589 + 4.168 \times 10^9 (1.365 \times 10^{-10} - r_j)$$

$$= 0.8278 - 4.168 \times 10^9 \, r_j \, ,$$

and the 'end points' errors are 3.32% for both end points. We, therefore, used (IV-41) in the present investigation.

The values reported for the carbon-carbon bond length in benzene by Almenningen et al. are 1.3974×10^{-10} and 1.3968×10^{-10} meters for an average value of 1.3971×10^{-10} meters [66]. Thus, we have

$$\text{(IV-42)} \qquad \$(\text{benzene}) = 0.2455 \, .$$

Division of (IV-41) by (IV-42) yields

$$\text{(IV-43)} \qquad \rho_j = 3.3719 - 1.6978 \times 10^{10} \, r_j \, ,$$

or

$$\text{(IV-44)} \qquad r_j = 1.9860 \times 10^{-10} - 5.8900 \times 10^{-11} \, \rho_j \, .$$

F. EIGENVALUE SECULAR EQUATIONS FOR POLYENES

A polyene is a topologically linear polymer in which the carbon–carbon bonds are alternately double and single bonds. Both end bonds are double bonds. We shall consider here only those cases in which all of the carbon atoms are co-planar, and the molecule has a center of symmetry or a central plane of symmetry. In these cases group theory permits the factoring of the determinantial secular equation of (IV-36) into two secular equations -- one for the symmetric wave functions and one for the antisymmetric wave functions. Thus, we may write

$$\text{(IV-45)} \qquad \begin{vmatrix} \lambda & \rho_1 & 0 & 0 & \cdots & & \\ \rho_1 & \lambda & \rho_2 & 0 & & & \\ \cdot & & \cdot & & & & \\ \cdot & & & \cdot & & & \\ \cdot & & & & \cdot & & \\ & & & & & \lambda & \rho_{n-1} \\ & & & & & \rho_{n-1} & \lambda \pm \rho_n \end{vmatrix} = 0.0 \quad ,$$

where ρ_j is really $\rho(j,\ j+1)$ and

$$\text{(IV-46)} \qquad \rho(j,\ j+1) = \frac{\$(j,\ j+1)}{\$} \quad .$$

The plus value at the n,n position is taken for the symmetric wave functions, and the negative value is taken for the antisymmetric wave functions.

By means of standard row operations the determinant of (IV-45) can be converted to the upper triangular form. When this is done the numerator of the n,n term, when set equal to zero, is the eigenvalue polynomial. If the first row is multiplied by $-\rho_1/\lambda$ and added to the second row, the new second row is

$$\text{(IV-47)} \qquad \rho_1 + \frac{-\rho_1(\lambda)}{\lambda} = 0.0, \quad \lambda - \frac{\rho_1(\rho_1)}{\lambda} = \frac{\lambda^2-\rho_1^2}{\lambda}, \ \rho_2, \ 0, \ \ldots \ .$$

The next three terms on the diagonal are

$$\text{(IV-48)} \qquad \lambda - \frac{\rho_2^2\lambda}{\lambda^2-\rho_1^2} = \frac{\lambda^3 - (\rho_1^2 + \rho_2^2)\lambda}{\lambda^2 - \rho_1^2} \ ,$$

$$\text{(IV-49)} \qquad \lambda - \frac{\rho_3^2(\lambda^2-\rho_1^2)}{\lambda^3 - (\rho_1^2+\rho_2^2)\lambda} = \frac{\lambda^4 - (\rho_1^2+\rho_2^2+\rho_3^2)\lambda^2 + \rho_1^2\rho_3^2}{\lambda^3 - (\rho_1^2+\rho_2^2)\lambda} \ ,$$

and

$$\text{(IV-50)} \qquad \lambda - \frac{\rho_4^2[\lambda^3 - (\rho_1^2+\rho_2^2)\lambda]}{\lambda^4 - (\rho_1^2+\rho_2^2+\rho_3^2)\lambda^2 + \rho_1^2\rho_3^2}$$

$$= \frac{\lambda^5 - (\rho_1^2+\rho_2^2+\rho_3^2+\rho_4^2)\lambda^3 + \{\rho_1^2\rho_3^2+\rho_4^2(\rho_1^2+\rho_2^2)\}\lambda}{\lambda^4 - (\rho_1^2+\rho_2^2+\rho_3^2)\lambda^2 + \rho_1^2\rho_3^2} \ .$$

If the specific term is to be the n,n term for the symmetric wave function determinant, the next higher ρ_j is added. Thus, (IV-51) $$\frac{\lambda^2-\rho_1^2}{\lambda} + \rho_2 = \frac{\lambda^2+\rho_2\lambda-\rho_1^2}{\lambda} ,$$

(IV-52) $$\frac{\lambda^3 - (\rho_1^2+\rho_2^2)\lambda}{\lambda^2-\rho_1^2} + \rho_3 = \frac{\lambda^3 + \rho_3\lambda^2 - (\rho_1^2+\rho_2^2)\lambda - \rho_1^2\rho_3}{\lambda^2-\rho_1^2} ,$$

(IV-53) $$\frac{\lambda^4 - (\rho_1^2+\rho_2^2+\rho_3^2)\lambda^2 + \rho_1^2\rho_2^2}{\lambda^3 - (\rho_1^2+\rho_2^2)\lambda} + \rho_4$$
$$= \frac{\lambda^4+\rho_4\lambda^3 - (\rho_1^2+\rho_2^2+\rho_3^2)\lambda^2 - \rho_4(\rho_1^2+\rho_2^2)\lambda + \rho_1^2\rho_3^2}{\lambda^3 - (\rho_1^2+\rho_2^2)\lambda} ,$$

and

(IV-54) $$\frac{\lambda^5 - (\rho_1^2+\rho_2^2+\rho_3^2)\lambda^3 + \{\rho_1^2\rho_3^2 + \rho_4^2(\rho_1^2+\rho_2^2)\}\lambda}{\lambda^4 - (\rho_1^2+\rho_2^2+\rho_3^2)\lambda^2 + \rho_1^2\rho_3^2} + \rho_5$$
$$= \Big[\lambda^5 + \rho_5\lambda^4 - (\rho_1^2+\rho_2^2+\rho_3^2+\rho_4^2)\lambda^3 - \rho_5(\rho_1^2+\rho_2^2+\rho_3^2)\lambda^2$$
$$+\{\rho_1^2\rho_3^2 + \rho_4^2(\rho_1^2+\rho_2^2)\lambda + \rho_1^2\rho_3^2\rho_5 \Big] \Big/$$
$$[\lambda^4 - (\rho_1^2+\rho_2^2+\rho_3^2)\lambda^2 + \rho_1^2\rho_3^2] \quad .$$

The eigenvalue polynomials, thus, are

(IV-55) $$\lambda^2+\rho_2 -\rho_1^2 = 0 ,$$

(IV-56) $$\lambda^3+\rho_3\lambda^2 - (\rho_1^2+\rho_2^2)\lambda - \rho_1^2\rho_3 = 0 ,$$

(IV-57) $$\lambda^4+\rho_4\lambda^3 - (\rho_1^2+\rho_2^2+\rho_3^2)\lambda^2 - \rho_4(\rho_1^2+\rho_2^2)\lambda + \rho_1^2\rho_3^2 = 0 ,$$

and

(IV-58) $$\lambda^5+\rho_5\lambda^4 - (\rho_1^2+\rho_2^2+\rho_3^2+\rho_4^2)\lambda^3 - \rho_5(\rho_1^2+\rho_2^2+\rho_3^2)\lambda^2 + \{\rho_1^2\rho_3^2 + \rho_4^2(\rho_1^2+\rho_2^2)\}\lambda + \rho_1^2\rho_3^2\rho_5 = 0 .$$

For ethylene itself the polynomial is

(IV-59) $$\lambda^2-\rho_1^2 = 0 .$$

By Descartes' rule of signs (IV-59) has one positive and one negative root; (IV-55) has one positive and one negative root; (IV-56) has one positive and two negative roots; (IV-57) has two positive and two negative roots; and (IV-58) has two positive and three negative roots. For convenience later we shall number the roots starting with the most negative. Thus, in general,

(IV-60) $$\lambda_1 < \lambda_2 < \lambda_3 < \cdots < \lambda_n$$

The latter roots are, of course, positive.

Any polynomial can be written as a product of factors. Thus,

(IV-61) $$\prod_{j=1}^{n} (\lambda-\lambda_j) = 0 .$$

For the first five degrees of polynomials these products are

(IV-62) $$(\lambda-\lambda_1)(\lambda-\lambda_2) = \lambda^2 - (\lambda_1+\lambda_2)\lambda + \lambda_1\lambda_2 = 0 ,$$

(IV-63) $$[\lambda^2-(\lambda_1+\lambda_2)\lambda + \lambda_1\lambda_2]\ (\lambda-\lambda_3)$$
$$= \lambda^3 - (\lambda_1+\lambda_2+\lambda_3)\lambda^2 + \{\lambda_1\lambda_2+\lambda_3(\lambda_1+\lambda_2)\}\lambda - \lambda_1\lambda_2\lambda_3 = 0 ,$$

(IV-64) $$[\lambda^3-(\lambda_1+\lambda_2+\lambda_3)\lambda^2 + \{\lambda_1\lambda_2+ \lambda_3(\lambda_1+\lambda_2)\}\lambda - \lambda_1\lambda_2\lambda_3]\ (\lambda-\lambda_4)$$
$$= \lambda^4 - (\lambda_1+\lambda_2+\lambda_3+\lambda_4)\lambda^3 + \{\lambda_1\lambda_2+\lambda_3(\lambda_1+\lambda_2) + \lambda_4(\lambda_1+\lambda_2+\lambda_3)\}\lambda^2$$
$$- \{\lambda_1\lambda_2\lambda_3+\lambda_4[\lambda_1\lambda_2+\lambda_3(\lambda_1+\lambda_2)]\}\lambda + \lambda_1\lambda_2\lambda_3\lambda_4 = 0 ,$$

and

(IV-65) $$[\lambda^4 - (\lambda_1+\lambda_2+\lambda_3+\lambda_4)\lambda^3 + \{\lambda_1\lambda_2+\lambda_3(\lambda_1+\lambda_2) + \lambda_4(\lambda_1+\lambda_2+\lambda_3)\}\lambda^2$$
$$- \{\lambda_1\lambda_2\lambda_3+\lambda_4[\lambda_1\lambda_2+\lambda_3(\lambda_1+\lambda_2)]\}\lambda + \lambda_1\lambda_2\lambda_3\lambda_4]\,(\lambda-\lambda_5)$$
$$= \lambda^5 - (\lambda_1+\lambda_2+\lambda_3+\lambda_4+\lambda_5)\lambda^4 + \{\lambda_1\lambda_2+\lambda_3(\lambda_1+\lambda_2) + \lambda_4(\lambda_1+\lambda_2+\lambda_3)$$
$$+ \lambda_5(\lambda_1+\lambda_2+\lambda_3+\lambda_4)\}\lambda^3 - \{\lambda_1\lambda_2\lambda_3+\lambda_4[\lambda_1\lambda_2+\lambda_3(\lambda_1+\lambda_2)]$$
$$+ \lambda_5[\lambda_1\lambda_2+\lambda_3(\lambda_1+\lambda_2) + \lambda_4(\lambda_1+\lambda_2+\lambda_3)]\}\lambda^2$$
$$+ \{\lambda_1\lambda_2\lambda_3\lambda_4+\lambda_5[\lambda_1\lambda_2\lambda_3+\lambda_4[\lambda_1\lambda_2+\lambda_3(\lambda_1+\lambda_2)]]\}\lambda - \lambda_1\lambda_2\lambda_3\lambda_4\lambda_5$$
$$= 0 .$$

If (IV-59) and (IV-62) are compared, the results are

(IV-66) $$\lambda_1\lambda_2 = -\rho_1^2 ,$$

and

(IV-67) $$\lambda_1+\lambda_2 = 0 \quad \text{or} \quad \lambda_2 = -\lambda_1 .$$

If (IV-55) and (IV-62) are compared, the results are

(IV-68) $$\rho_2 = -(\lambda_1+\lambda_2) ,$$

and

(IV-69) $$\rho_1^2 = -\lambda_1\lambda_2 .$$

If (IV-57) and (IV-63) are compared, the results are

(IV-70) $$\rho_3 = -(\lambda_1 + \lambda_2 + \lambda_3) ,$$

(IV-71) $$\rho_1^2 + \rho_2^2 = -\{\lambda_1\lambda_2 + \lambda_3(\lambda_1+\lambda_2)\}$$

and

(IV-72) $$\rho_1^2\rho_3 = \lambda_1\lambda_2\lambda_3 .$$

If (IV-57) and (IV-64) are compared, the results are

(IV-73) $$\rho_4 = -(\lambda_1 + \lambda_2 + \lambda_3 + \lambda_4) ,$$

(IV-74) $$\rho_1^2+\rho_2^2+\rho_3^2 = -\{\lambda_1\lambda_2 + \lambda_3(\lambda_1+\lambda_2) + \lambda_4(\lambda_1+\lambda_2+\lambda_3)\} ,$$

(IV-75) $$\rho_4(\rho_1^2+\rho_2^2) = \lambda_1\lambda_2\lambda_3 + \lambda_4[\lambda_1\lambda_2 + \lambda_3(\lambda_1+\lambda_2)] \quad ;$$

and

(IV-76) $$\rho_1^2\rho_3^2 = \lambda_1\lambda_2\lambda_3\lambda_4 \quad .$$

Finally, if (IV-58) and (IV-65) are compared, the results are

(IV-77) $$\rho_5 = -(\lambda_1+\lambda_2+\lambda_3+\lambda_4+\lambda_5) \quad ,$$

(IV-78) $$\rho_1^2+\rho_2^2+\rho_3^2+\rho_4^2 = -\{\lambda_1\lambda_2 + \lambda_3(\lambda_1+\lambda_2) + \lambda_4(\lambda_1+\lambda_2+\lambda_3) + \lambda_5(\lambda_1+\lambda_2+\lambda_3+\lambda_4)\} \quad ,$$

(IV-79) $$\rho_5(\rho_1^2+\rho_2^2+\rho_3^2) = \lambda_1\lambda_2\lambda_3 + \lambda_4[\lambda_1\lambda_2 + \lambda_3(\lambda_1+\lambda_2)] + \lambda_5[\lambda_1\lambda_2 + \lambda_3(\lambda_1+\lambda_2) + \lambda_4(\lambda_1+\lambda_2+\lambda_3)] \quad ,$$

(IV-80) $$\rho_1^2\rho_3^2 + \rho_4^2(\rho_1^2+\rho_2^2) = \lambda_1\lambda_2\lambda_3\lambda_4 + \lambda_5[\lambda_1\lambda_2\lambda_3 + \lambda_4[\lambda_1\lambda_2 + \lambda_3(\lambda_1+\lambda_2)]] \quad ,$$

and

(IV-81) $$\rho_1^2\rho_3^2\rho_5 = -\lambda_1\lambda_2\lambda_3\lambda_4\lambda_5$$

For (IV-68) and (IV-69) the equations are invariant if ρ_2, λ_1 and λ_2 are replaced by their additive inverses. For (IV-70), (IV-71) and (IV-72) the equations are invariant if ρ_3, λ_1, λ_2 and λ_3 are replaced by their additive inverses. Similarly, for (IV-73), (IV-74), (IV-75) and (IV-76) the equations are invariant if ρ_4, λ_1, λ_2, λ_3 and λ_4 are replaced by their additive inverses. Finally, (IV-77) through (IV-81) are invariant if ρ_5 and the λ_j's are replaced by their additive inverses. Thus, the positive roots of the symmetric wave functions determinant are the negative of the negative roots of the anti-symmetric wave functions determinant. This is a generally valid theorem. We shall, however, not give the proof here. In what follows below we shall use the convention

$$\text{(IV-82)} \qquad \bar{\lambda}_j = -\lambda_j \ .$$

In this way we shall need to consider only the symmetric wave functions determinants.

[It should be noted that much of the mathematics developed in this and subsequent SECTIONS was necessary in this study. As a result of administrative difficulties the contract for this study was not awarded until the study was almost complete. As a result no funds were available for computer calculations. Most of the work in this study was done on a TI-59 programmable calculator. It was, therefore, necessary for us to develop many theorems from the theory of equations, a branch of mathematics which computers have made obsolete.]

G. CLAUSTROPHOBIC ENERGY THEOREM FOR CONJUGATED SYSTEMS.

1. INTRODUCTION

In a bonding σ-orbital the electrons are 'concentrated' along the axis between the two atoms as we have indicated for the H_2^+ and H_2 cases. Classically, the potential energy of such a system would decrease without limit as the distances between the particles decrease. Quantum mechanically such a collapse of the universe to a point cannot occur. As the volume in which a particle is effectively contained decrases the claustrophobic energy increases. The balancing of these opposing effects results in the σ-bonds having definite equilibrium bond length values (which are, of course, functions of temperature). As we have indicated above the σ-bond is, thus, an oscillator. For <u>small</u> deviations from the equilibrium bond lengths the oscillator can be treated as though it were a harmonic oscillator. Actually the σ-bond oscillators are anharmonic as is well known from infrared spectral analyses.

When π-orbitals are also present, the σ-equilibrium is perturbed in at least two ways. Saturated carbon atoms use hybridized sp^3-orbitals to form the σ-orbitals. The carbon atoms involved with π-orbitals, however, use sp^2-orbitals (double bonds) or sp-orbitals (triple bonds) to form the σ-orbitals. Thus, we should expect different values for the force constants for the harmonic oscillators in the three cases. Furthermore, the π-electrons introduce an additional negative potential energy term. Since these electrons are not 'concentrated' along the axis between the bonded atoms, the π-potential energy will be smaller in magnitude than the corresponding σ-electron potential energy. This factor is reflected in the fact that the bond energy for a carbon-carbon single bond is 83.1 kcal·mole^{-1} (347.7 kJoules·mole^{-1}), whereas those for the double and triple bonds are 147 and 194 kcal·mole^{-1} (615.0 and 811.7 kJoules·mole^{-1}), respectively [67]. A single π-bond contributes 63.9 kcal·bond^{-1}·mole^{-1} (267.4 kJoules·bond·mole^{-1}) whereas a pair of π-bonds (triple bond) contributes 55.4 kcal·bond^{-1}·mole^{-1} (232 kJoules·bond^{-1}·mole^{-1}).

The presence of this additional potential energy term also results in the equilibrium bond lengths being smaller. Thus, the carbon-carbon bond length is 1.536×10^{-10} meters in ethane [68], 1.3971×10^{-10} meters in benzene [66] 1.334×10^{-10} meters in ethylene [69] and 1.205×10^{-10} meters in acetylene [70].

In the present treatment we shall represent the σ-bonds by harmonic oscillators. The energy of the π-electrons will be obtained by semi-empirical LCAO-MO (Linear Combination of Atomic Orbitals - Molecular Orbital) theory including adjacent overlap. The various bond lengths are then obtained by minimizing the energy of the molecule with respect to the bond lengths.

2. THE σ-BOND ENERGY

If the deviations from the equilibrium bond length of a σ-bond are sufficiently small, the claustrophobic energy-bond length function may be approximated by that of a harmonic oscillator

$$E_k(\text{harmonic oscillator}) = \frac{1}{2}\, k_e(r-r_e)^2 \,, \tag{IV-83}$$

where k_e is the 'force constant' and r_e is the equilibrium bond length. For the carbon–carbon sp^3–sp^3 σ-bond k_e may be taken as 4.9×10^2 Newtons·meter^{-1}·bond^{-1} [71].

A more accurate value of E_k can be obtained by using the anharmonic oscillator equation of Morse [72].

$$E_k \doteq D_e[1 - \exp\{-b(r-r_e)\}]^2 \,. \tag{IV-84}$$

D_e is the zero point energy plus $1/2\, h\nu_e$, where ν_e is the harmonic oscillator frequency. The k_e of (IV-83) and the b of (IV-84) are related by

$$k_e = 2b^2\, D_e \,. \tag{IV-85}$$

In the present treatment, as we have indicated before, we shall use (IV-83). The total σ-bond energy will be taken as

$$E_\sigma(\text{total}) = \frac{k_e}{2}\,(r-r_e)^2 - D_o \,, \tag{IV-86}$$

where D_o is the zero point energy.

3. THE π-BOND ENERGY

The derivation of the eigen-determinant by the semi-empirical LCAO – MO is given in the APPENDIX. If we replace E_k in (A-48) by ε_k, we have

(IV-87) $$\varepsilon_k = \not{q} - \frac{\gamma\lambda_k}{1 - \lambda_k \$} .$$

Equation (A-49) gives the value of γ used in previous studies. In this study we shall find it convenient to use $-4\gamma/k_e$ as the empirically determined parameter instead.

If there are $2n$ π-electrons and p σ-bonds in the π-lattice (the set of atoms involved with π-orbitals in the specific molecular configuration), the 'total' energy is

(IV-88) $$\begin{aligned} E_T &= E_\pi + \sum_{j=1}^{p} E_\sigma(j) \\ &= 2n\not{q} - 2\gamma \sum_{k=1}^{n} \frac{\lambda_k}{1 - \lambda_k \$} \\ &\qquad + \frac{k_e}{2} \sum_{j=1}^{p} (r_j - r_e)^2 - pD_o \quad , \end{aligned}$$

where r_j is the length of the j-th bond. Since neither $2n\not{q}$ nor pD_o are functions of the r_j's, (IV-88) may be rewritten as

(IV-89) $$\begin{aligned} \Delta E_T &= E_T - (2nq - pD_o) \\ &= -2\gamma \sum_{k=1}^{n} \frac{\lambda_k}{1 - \lambda_k \$} + \frac{k_e}{2} \sum_{j=1}^{p} (r_j - r_e)^2 \\ &= -2\gamma \sum_{k=1}^{n} \frac{\lambda_k}{1 - \lambda_k \$} + \frac{k_e (5.8900 \times 10^{-11})^2}{2} \sum_{j=1}^{p} (\rho_j - \rho_e)^2 \end{aligned}$$

[by (IV-44)]

or

$$\text{(IV-90)} \qquad \Delta E_T' = \frac{2\ E_T}{k_e(5.8900 \times 10^{-11})^2}$$

$$= f \sum_{k=1}^{n} \frac{\lambda_k}{1 - \lambda_k \$} + \sum_{j=1}^{p} (\rho_j - \rho_e)^2 \quad ,$$

where

$$\text{(IV-91)} \qquad f = \frac{-4\gamma}{k_e(5.8900 \times 10^{-11})^2} \ .$$

In the present treatment both f and ρ_e are parameters which are evaluated from experimental data, a topic to which we now turn.

V. SMALL MOLECULE ANALYSES

A. BUTADIENE

Since we have two parameters to evaluate, we must take the case of a molecule for which the symmetry factored eigen-determinant is at least a 2 × 2. The eigen-determinant for butadiene is a 2 × 2. It is, therefore, a logical case to consider. By (IV-68) and (IV-69)

$$\lambda_2 = \frac{-\rho_1^2}{\lambda_1} ,$$

$$-\rho_2 = \lambda_1 - \frac{\rho_1^2}{\lambda_1} ,$$

$$-\rho_2\lambda_1 = \lambda_1^2 - \rho_1^2 ,$$

$$\lambda_1^2 + \rho_2\lambda_1 - \rho_1^2 = 0 ,$$

or

$$\lambda_1 = \frac{-\rho_2 \pm \sqrt{\rho_2^3 + 4\rho_1^2}}{2} . \tag{V-1}$$

The two values of (V-1) are actually λ_1 and λ_2. We now invoke (IV-82). Thus,

$$\lambda_1 = \frac{-\rho_2 - \sqrt{\rho_2^2 + 4\rho_1^2}}{2} , \tag{V-2}$$

and

$$\bar{\lambda}_2 = \frac{\rho_2 - \sqrt{\rho_2^2 + 4\rho_1^2}}{2} . \tag{V-3}$$

Since ρ_1 represents the 'double' bonds in butadiene, and since there are two 'double' bonds and one 'single' bond, (IV-90) is for the butadiene case

$$\text{(V-4)} \qquad \Delta E_T' = f\left[\frac{-(\rho_2 + \sqrt{\rho_2^2 + 4\rho_1^2})/2}{1 - 0.2455\{-(\rho_2 + \sqrt{\rho_2^2 + 4\rho_1^2})/2\}} + \frac{(\rho_2 - \sqrt{\rho_2^2 + 4\rho_1^2})/2}{1 - 0.2455\{(\rho_2 - \sqrt{\rho_2^2 + 4\rho_1^2})/2\}}\right] + 2(\rho_1-\rho_e)^2 + (\rho_2-\rho_e)^2 ,$$

where (IV-42) has been taken as the value of $\$$. We shall now rearrange (V-4) to a somewhat more convenient form, take the partial derivatives of $\Delta E_T'$ with respect to ρ_1 and ρ_2, and set the derivatives equal to zero. Since the mathematics is straight forward, we shall present it without comment.

$$\Delta E_T' = f\left[\frac{-\rho_2 - \sqrt{\rho_2^2 + 4\rho_1^2}}{2 + 0.2455\ \rho_2 + 0.2455\sqrt{\rho_2^2 + 4\rho_1^2}} + \frac{\rho_2 - \sqrt{\rho_2^2 + 4\rho_1^2}}{2 - 0.2455\ \rho_2 + 0.2455\ \sqrt{\rho_2^2 + 4\rho_1^2}}\right]$$

$$+ 2(\rho_1-\rho_e)^2 + (\rho_2-\rho_e)^2$$

(continued)

$$= f\left[\frac{-\rho_2 - \sqrt{\rho_2^2 + 4\rho_1^2}}{(2 + 0.2455\sqrt{\rho_2^2 + 4\rho_1^2}) + 0.2455\ \rho_2}\right.$$

$$\left.+ \frac{\rho_2 - \sqrt{\rho_2^2 + 4\rho_1^2}}{(2 + 0.2455\sqrt{\rho_2^2 + 4\rho_1^2}) - 0.2455\ \rho_2}\right]$$

$$+ 2(\rho_1-\rho_e)^2 + (\rho_2-\rho_e)^2$$

$$= f\left[\frac{-2\sqrt{\rho_2^2 + 4\rho_1^2}\ (2 + 0.2455\sqrt{\rho_2^2 + 4\rho_1^2}) + 2 \times 0.2455\ \rho_2^2}{(2 + 0.2455)\sqrt{\rho_2^2 + 4\rho_1^2})^2 - (0.2455\ \rho_2)^2}\right]$$

$$+ 2(\rho_1-\rho_e)^2 + (\rho_2-\rho_e)^2$$

$$= f\left[\frac{-4\sqrt{\rho_2^2 + 4\rho_1^2} - 2 \times 0.2455(\rho_2^2 + 4\rho_1^2) + 2 \times 0.2455\ \rho_2^2}{4 + 4 \times 0.2455\sqrt{\rho_2^2 + 4\rho_1^2} + (0.2455)^2\ (\rho_2^2 + 4\rho_1^2) - (0.2455\ \rho_2)^2}\right]$$

$$+ 2(\rho_1-\rho_e)^2 + (\rho_2-\rho_e)^2$$

$$= f\left[\frac{-4\sqrt{\rho_2^2 + 4\rho_1^2} - 8 \times 0.2455\ \rho_1^2}{4 + 4 \times 0.2455\sqrt{\rho_2^2 + 4\rho_1^2} + 4 \times (0.2455)^2\ \rho_1^2}\right]$$

$$+ 2(\rho_1-\rho_e)^2 + (\rho_2-\rho_e)^2 \quad ,$$

$$\Delta E_T' = -f\left[\frac{\sqrt{\rho_2^2 + 4\rho_1^2} + 2 \times 0.2455\ \rho_1^2}{1 + 0.2455\sqrt{\rho_2^2 + 4\rho_1^2} + (0.2455)^2\ \rho_1^2}\right]$$

$$+ 2(\rho_1-\rho_e)^2 + (\rho_2-\rho_e)^2$$

$$= -f\left[\frac{\sqrt{\rho_2^2 + 4\rho_1^2} + 0.4910\ \rho_1^2}{1 + 0.2455\sqrt{\rho_2^2 + 4\rho_1^2} + 6.027 \times 10^{-2}\ \rho_1^2}\right]$$

$$+ 2(\rho_1-\rho_e)^2 + (\rho_2-\rho_e)^2 \quad ,$$

$$\frac{\partial \Delta E_T'}{\partial \rho_1} = 4(\rho_1-\rho_e) - f\left[\frac{\frac{1}{2}\ (4)\ \ (2\rho_1)/\sqrt{\rho_2^2 + 4\rho_1^2} + 2 \times 0.4910\ \rho_1}{1 + 0.2455\sqrt{\rho_2^2 + 4\rho_1^2} + 6.0270 \times 10^{-2}\ \rho_1^2}\right.$$

$$- \left\{\sqrt{\rho_2^2 + 4\rho_1^2} + 0.4910\ \rho_1^2\right\}$$

$$\cdot \left\{\frac{1}{2}\ (4)\ \ (2\rho_1)\ \ (0.2455)/\sqrt{\rho_2^2 + 4\rho_1^2} + 2 \times 6.0270 \times 10^{-2}\rho_1\right\}$$

$$\left. \cdot \left\{1 + 0.2455\sqrt{\rho_2^2 + 4\rho_1^2} + 6.0270 \times 10^{-2}\ \rho_1^2\right\}^{-2}\right] ,$$

$$\frac{\partial \Delta E_T'}{\partial \rho_2} = 2(\rho_2-\rho_e) - f\left[\frac{\frac{1}{2}(2\rho_2)/\sqrt{\rho_2^2+4\rho_1^2}}{1+0.2455\sqrt{\rho_2^2+4\rho_1^2}+6.0270\times 10^{-2}\rho_1^2}\right.$$

$$-\left\{\sqrt{\rho_2^2+4\rho_1^2}+0.4910\ \rho_1^2\right\}$$

$$\cdot\left\{\frac{1}{2}(2\rho_2)\ (0.2455)/\sqrt{\rho_2^2+4\rho_1^2}\right\}$$

$$\left.\cdot\left\{1+0.2455\sqrt{\rho_2^2+4\rho_1^2}+6.0270\times 10^{-2}\ \rho_1^2\right\}^{-2}\right] .$$

For 1,3-butadiene the experimental values of the 'single' and 'double' bond lengths are 1.467×10^{-10} meters and 1.343×10^{-10} meters, respectively [73]. By (IV-43) these bond lengths correspond to

(V-5)
$$\rho_1 = 3.3719 - 1.6978 \times 10^{10} \times 1.343 \times 10^{-10}$$
$$= 1.0918$$

and

(V-6)
$$\rho_2 = 3.3719 - 1.6978 \times 10^{10} \times 1.467 \times 10^{-10}$$
$$= 0.8812 .$$

Thus,

(V-7)
$$\left.\frac{\partial \Delta E_T'}{\partial \rho_1}\right|_{\substack{\rho_1=1.0918\\ \rho_2=0.8812}} = 4(1.0918 - \rho_e) - 1.1400\ f$$

$$= 4.3672 - 4\rho_e - 1.1400\ f$$

$$= 0.00$$

and

(V-8)
$$\left.\frac{\partial \Delta E_T'}{\partial \rho_2}\right|_{\substack{\rho_1=1.0918\\ \rho_2=0.8812}} = 2(0.8812 - \rho_e) - 0.1276\ f$$

$$= 1.7624 - 2\rho_e - 0.1276\ f$$

$$= 0.00\ .$$

From these equations we obtain

$$0 = 4.3672 - 4\rho_e - 1.1400\ f$$

$$0 = 3.5248 - 4\rho_e - 0.2552\ f$$

$$0.8848\ f = 0.8424$$

or

(V-9)
$$f = 0.9521\ .$$

By (V-7)

$$4\rho_e = 4.3672 - 1.1400\ (0.9521)$$

or

(V-10) $$\rho_e = 0.8205\ .$$

By (IV-43)

(V-11) $$\begin{aligned} r_e &= 1.9860 \times 10^{-10} - 5.8900 \times 10^{-11}\ (0.8205) \\ &= 1.5027 \times 10^{-10} \text{ meters}\ . \end{aligned}$$

As we have noted above the experimental value for the carbon-carbon bond length in ethane is 1.536×10^{-10} meters. If we identify r_e with the ethane value, it is in error by only 2.2%. Actually the identification is not correct since the σ-bond in ethane is $sp^3 - sp^3$ where as r_e is for a σ-bond with $sp^2 - sp^2$ hybridization.

B. ETHYLENE

With the values of (V-9) and (V-10) equation (IV-90) now becomes

(V-12) $$\Delta E_T' = 0.9521 \sum_{k=1}^{n} \frac{\lambda_k}{1 - 0.2455\ \lambda_k} + \sum_{j=1}^{p} (p_j - 0.8205)^2\ .$$

By (IV-66) and (IV-67)

(V-13) $$\rho_1 = -\lambda_1\ .$$

Thus,

$$\text{(V-14)} \qquad \Delta E_T'(\text{ethylene}) = \frac{0.9521\ \lambda_1}{1 - 0.2455\ \lambda_1} + (\lambda_1 + 0.8205)^2 \ .$$

Although this equation is so simple that there is no difficulty in using the minimization technique of differential calculus, we developed a machine procedure for the TI-59. Since our goal is to study polymers, the calculus technique is not really a viable choice as a general procedure. In the machine procedure we calculate $\Delta E_T'$ for various values of λ_1 and choose the value which gives the lowest value of $\Delta E_T'$. The minimum value of $\Delta E_T'$, -0.746720, is obtained with $\lambda_1 = -1.114$. Thus,

$$\text{(V-15)} \qquad \rho_1 = 1.114$$

and by (IV-43)

$$\text{(V-16)} \qquad r_1 = 1.9860 \times 10^{-10} - 5.8900 + 10^{-11} \times 1.114$$

$$= 1.3299 \times 10^{-10} \text{ meters} \ .$$

As we have noted above the experimental value for ethylene is 1.334×10^{-10} meters. Thus, the error of the calculated value is 0.31%.

C. HEXATRIENE

In 1,3,5,-hexatriene the outer 'double' bonds may be trans- or cis-relative to the central 'double' bond. The bond lengths for both cases have been determined experimentally. For the trans-form the outer 'double' bond length, the 'single' bond length and the inner 'double' bond length are 1.337×10^{-10}, 1.457×10^{-10} and 1.367×10^{-10} meters, respecitvely [74]. For the cis-form the corresponding values are 1.336×10^{-10}, 1.462×10^{-10} and 1.362×10^{-10} meters, respectively [75]. Since we have neglected non-adjacent interactions in the present investigation, we cannot distinguish between the two forms. We shall, therefore, use the averages of the two sets of values — 1.3365×10^{-10}, 1.4595×10^{-10} and 1.3645×10^{-10} meters, respectively.

From (IV-70) through (IV-72) we have

$$\rho_3 = \bar{\lambda}_3 - \lambda_1 - \lambda_2 = A \, , \tag{V-17}$$

$$\rho_1^2+\rho_2^2 = \bar{\lambda}_3(\lambda_1+\lambda_2) - \lambda_1\lambda_2 = B \, , \tag{V-18}$$

$$\rho_1^2\rho_3 = -\lambda_1\lambda_2\bar{\lambda}_3 = C \, , \tag{V-19}$$

(V-20)
$$\begin{aligned}\rho_1^2 &= C/A \\ &= D\ ,\end{aligned}$$

(V-21)
$$\rho_1 = D^{1/2}\ ,$$

(V-22)
$$\rho_2^2 = B\text{-}D\ ,$$

and

(V-23)
$$\rho_2 = (B\text{-}D)^{1/2}\ .$$

Thus, (V-12) now becomes

(V-24)
$$\begin{aligned}\Delta E_T'(\text{hexatriene}) &= 0.9521\left[\frac{\lambda_1}{1 - 0.2455\ \lambda_1} + \frac{\lambda_2}{1 - 0.2455\ \lambda_2} + \frac{\bar{\lambda}_3}{1 - 0.2455\ \bar{\lambda}_3}\right] \\ &\quad + 2(\rho_1 - 0.8205)^2 + 2(\rho_2 - 0.8205)^2 + (\rho_3 - 0.8205)^2 \\ &= 0.9521\left[\frac{\lambda_1}{1 - 0.2455\ \lambda_1} + \frac{\lambda_2}{1 - 0.2455\ \lambda_2} + \frac{\bar{\lambda}_3}{1 - 0.2455\ \bar{\lambda}_3}\right] \\ &\quad + 2(D^{1/2} - 0.8205)^2 + 2(\{B\text{-}D\}^{1/2} - 0.8205)^2 \\ &\quad + (A - 0.8205)^2\ .\end{aligned}$$

The minimum value of $\Delta E_T'$, -2.355237086, is obtained with

(V-25) $$\lambda_1 = -1.780$$

$$\lambda_2 = -0.556$$

$$\bar{\lambda}_3 = -1.270 \; .$$

Thus,

(V-26) $$\rho_1 = 1.0859$$

$$\rho_2 = 0.8933$$

$$\rho_3 = 1.0660 \; ,$$

and by (IV-43)

(V-27) $$r_1 = 1.9860 \times 10^{-10} - 5.8900 \times 10^{-11} \times 1.0859$$

$$= 1.3464 \times 10^{-10} \text{ meters} \; ,$$

(V-28) $$r_2 = 1.9860 \times 10^{-10} - 5.8900 \times 10^{-11} \times 0.8933$$

$$= 1.4598 \times 10^{-10} \text{ meters}$$

and

(V-29) $$r_3 = 1.9860 \times 10^{-10} - 5.8900 \times 10^{-11} \times 1.0660$$

$$= 1.3581 \times 10^{-10} \text{ meters} \; .$$

With respect to the averaged experimental values the errors in the calculated values are 0.74%, 0.02% and 0.47%, respectively.

D. OCTATETRAENE

From (IV-73) through (IV-76) we have

$$\begin{aligned} \rho_4 &= \bar{\lambda}_4 + \bar{\lambda}_3 - \lambda_2 - \lambda_1 \\ &= A\ , \end{aligned} \tag{V-30}$$

$$\begin{aligned} \rho_1^2+\rho_2^2+\rho_3^2 &= (\lambda_1+\lambda_2)\ (\bar{\lambda}_3+\bar{\lambda}_4) - \lambda_1\lambda_2 - \bar{\lambda}_3\bar{\lambda}_4 \\ &= B\ , \end{aligned} \tag{V-31}$$

$$\begin{aligned} \rho_4(\rho_1^2+\rho_2^2) &= (\lambda_1+\lambda_2)\ \bar{\lambda}_3\bar{\lambda}_4 - \lambda_1\lambda_2\ (\bar{\lambda}_3+\bar{\lambda}_4) \\ &= C\ , \end{aligned} \tag{V-32}$$

$$\begin{aligned} \rho_1^2\rho_3^2 &= \lambda_1\lambda_2\bar{\lambda}_3\bar{\lambda}_4 \\ &= D\ , \end{aligned} \tag{V-33}$$

$$\begin{aligned} \rho_1^2+\rho_2^2 &= C/A \\ &= E\ , \end{aligned} \tag{V-34}$$

$$\begin{aligned} \rho_3^2 &= B-E \\ &= F\ , \end{aligned} \tag{V-35}$$

$$\rho_3 = F^{1/2}\ , \tag{V-36}$$

(V-37) $$\rho_1^2 = D/F$$

$$= G \, ,$$

(V-38) $$\rho_1 = G^{1/2}$$

(V-39) $$\rho_2^2 = E - G$$

$$= H$$

and

(V-40) $$\rho_2 = H^{1/2} \, .$$

Thus, (V-12) becomes

(V-41) $$\Delta E_T'(\text{octatetraene})$$

$$= 0.9521 \Big[\lambda_1/(1 - 0.2455\ \lambda_1)$$

$$+ \lambda_2/(1 - 0.2455\ \lambda_2)$$

$$+ \lambda_3/(1 - 0.2455\ \lambda_3)$$

$$+ \lambda_4/(1 - 0.2455\ \lambda_4) \Big]$$

$$+ 2(G^{1/2} - 0.8205)^2$$

$$+ 2(H^{1/2} - 0.8205)^2$$

$$+ 2(F^{1/2} - 0.8205)^2$$

$$+ (A - 0.8205)^2 \, .$$

The minimum value of $\Delta E_T'$, -3.16850039, is obtained with

(V-42) $\lambda_1 = -1.849$

$\lambda_2 = -1.033$

$\bar{\lambda}_3 = -0.449$

$\bar{\lambda}_4 = -1.524$.

Thus,

(V-43) $\rho_1 = 1.0823$

$\rho_2 = 0.8971$

$\rho_3 = 1.0563$

$\rho_4 = 0.9090$

and by (IV-43)

(V-44) $r_1 = 1.3485 \times 10^{-10}$ meters

$r_2 = 1.4576 \times 10^{-10}$ meters

$r_3 = 1.3638 \times 10^{-10}$ meters

$r_4 = 1.4506 \times 10^{-10}$ meters .

At this point in our study we had three choices -- continue developing the algebra for each molecule individually, develop a set of general recursion formulae or by means of a set of computer programs:

1. Choose a set of ρ_j's.
2. Using these ρ_j's calculate the eigenvalues of (IV-45).
3. Using the ρ_j^2, the λ_k's and (V-12) calculate $\Delta E_T'$.
4. Using a minimization program vary the values of the ρ_j's and with steps 2 and 3 find the minimum value of $\Delta E_T'$.

Since at this juncture we did not yet have any computer funds, we proceeded to develop general recursion formulae. We shall, therefore, now turn to a discussion of the theory of equations theorems which we developed.

VI. GENERAL RECURSION FORMULAE

A. THE ENERGY EQUATION

Let m be the number of electrons in π-lattice, and let n be the number of bonds in the π-lattice. The reduced form of the total energy is given by

$$\text{(VI-1)} \qquad \Delta E_T' = 0.47605 \sum_{i=1}^{m} \lambda_i/(1 - 0.2455\,\lambda_i) + \sum_{j=1}^{n} (\rho_j - 0.8205)^2 \ .$$

This equation is more general than (V-12) since it is not assumed that all electrons are paired. Using the spectral data for benzene we have found that the relation between ΔE_T and $\Delta E_T'$ is

$$\text{(VI-2)} \qquad \Delta E_T = 7.969 \times 10^{-19}\, \Delta E_T' \text{ Joules}\cdot\text{molecule}^{-1} \ .$$

For polyenes which are neutral m is also equal to the number of carbon atoms in the π-lattice. There are, therefore, m-1 bonds, of which there are (m-2)/2 paired bonds and one unpaired bond when symmetry factoring is applicable. In the <u>ground state</u> of the molecule there are two electrons per π-orbital. Thus,

$$\text{(IV-3)} \qquad \Delta E_T' = 0.9521 \sum_{i=1}^{m/2} \lambda_i/(1 - 0.2455\,\lambda_i)$$
$$+ 2 \sum_{j=1}^{(m-2)/2} (\rho_j - 0.8205)^2 + (\rho_{m/2} - 0.825)^2 \ .$$

We now take

(VI-4) $$n = m/2 ,$$

and

(VI-5) $$\Delta E_T' = 0.9521 \sum_{i=1}^{n} \lambda_i/(1 - 0.2455\ \lambda_i) + 2 \sum_{j=1}^{n-1} (\rho_j - 0.8205)^2 + (\rho_n - 0.8205)^2 .$$

When symmetry factoring is used, two secular determinants are generated, the '$\lambda+\rho_n$' determinant and the '$\lambda-\rho_n$' determinant. Each of the determinants yields n values of ρ. As we have indicated in SECTION IV.F the values of λ from the second determinant are the negative of those from the first determinant. We may, therefore, restrict our considerations to the '$\lambda+\rho_n$' determinant if the signs are changed for the positive values of λ for the first summation in (VI-5).

Thus, if p is the number of λ's with positive values,

(VI-6) $$\Delta E_T' = 0.9521 \sum_{i=1}^{n-p} \lambda_i/(1 - 0.2455\ \lambda_i) - 0.9521 \sum_{i=n+1-p}^{n} \lambda_i/(1 + 0.2455\ \lambda_i) + 2 \sum_{j=1}^{n-1} (\rho_j - 0.8205)^2 + (\rho_n - 0.8205)^2 .$$

In what follows we shall find it convenient to take

(VI-7) $$\mu_i = - \lambda_i .$$

Thus, (VI-6) becomes

$$\text{(VI-8)} \qquad \Delta E_T' = 0.9521 \sum_{i=n+1-p}^{n} \mu_i/(1 - 0.2455\,\mu_i) - 0.9521 \sum_{i=1}^{n-p} \mu_i/(1+0.2455\,\mu_i)$$

$$+ 2 \sum_{j=1}^{n-1} (\rho_j - 0.8205)^2 + (\rho_n - 0.8205)^2 .$$

The goal of EBL theory is to find the values of the ρ's which minimize $\Delta E_T'$. In order to do this it is necessary to express the μ's as functions of the ρ's or, as we shall do here, express the ρ's as functions of the μ's.

B. THE EIGENVALUE POLYNOMIAL IN TERMS OF THE μ's

The eigenvalue polynomial may be written as

$$\text{(VI-9)} \qquad \lambda^n + a_1\,\lambda^{n-1} + \cdots + a_n\,\lambda^0 = 0 \ ,$$

or, if we take

$$\text{(VI-10)} \qquad a_0 = +1 \ ,$$

$$\text{(VI-11)} \qquad \sum_{i=0}^{n} a_i\,\lambda^{n-i} = 0 \ .$$

If $\lambda_1, \ldots, \lambda_i, \ldots, \lambda_n$ are the roots of the polynomial,

$$\text{(VI-12)} \qquad \prod_{i=1}^{n} (\lambda - \lambda_i) = 0 \ ,$$

or by (VI-7)

(VI-13) $$\prod_{i=1}^{n} (\lambda+\mu_i) = 0 \quad .$$

The results of the first few multiplications in (VI-13) are

$$(\lambda+\mu_2)(\lambda+\mu_1) = \lambda^2 + (\mu_2+\mu_1)\lambda + \mu_2\mu_1 \quad ,$$

$$(\lambda+\mu_3)(\lambda+\mu_2)(\lambda+\mu_1) = \lambda^3 + (\mu_3+\mu_2+\mu_1)\lambda^2$$
$$+ [\mu_3(\mu_2+\mu_1) + \mu_2(\mu_1)]\lambda + \mu_3\mu_2\mu_1 \quad ,$$

and

$$(\lambda+\mu_4)(\lambda+\mu_3)(\lambda+\mu_2)(\lambda+\mu_1)$$
$$= \lambda^4 + (\mu_4+\mu_3+\mu_2+\mu_1)\lambda^3$$
$$+ [\mu_4(\mu_3+\mu_2+\mu_1) + \mu_3(\mu_2+\mu_1) + \mu_2(\mu_1)]\lambda^2$$
$$+ [\mu_4\{\mu_3(\mu_2+\mu_1) + \mu_2(\mu_1)\} + \mu_3\{\mu_2(\mu_1)\}]\lambda$$
$$+ \mu_4\mu_3\mu_2\mu_1 \quad .$$

The values of the a(i,n)'s of (IV-11) are generated by the following algorithm

(IV-14)
$$a(0,n) = 1$$
$$a(i,n) = 0 \;, \qquad i > n$$
$$a(i,n) = \mu_n\, a(i-1, n-1) + a(i, n-1) \quad .$$

The use of this algorithm is exemplified by

$$a(1,1) = \mu_1 \, a(0,0) + a(1,0)$$

$$= \mu_1 \qquad [a(0,0) = 1,\ a(1,0) = 0] \ ,$$

$$a(1,2) = \mu_2 \, a(0,1) + a(1,1)$$

$$= \mu_2 + \mu_1 \ ,$$

$$a(2,2) = \mu_2 \, a(1,1) + a(2,1)$$

$$= \mu_2(\mu_1) \qquad [a(2,1) = 0] \ ,$$

$$a(1,3) = \mu_3 \, a(0,2) + a(1,2)$$

$$= \mu_3 + \mu_2 + \mu_1 \ ,$$

$$a(2,3) = \mu_3 \, a(1,2) + a(2,2)$$

$$= \mu_3(\mu_2 + \mu_1) + \mu_2(\mu_1) \ ,$$

and

$$a(3,3) = \mu_3 \, a(2,2) + a(3,2)$$

$$= \mu_3(\mu_2)\ (\mu_1) \ .$$

C. THE EIGENVALUE POLYNOMIAL IN TERMS OF THE ρ's

In terms of the ρ_j's the secular determinant is given by (IV-45) with $\lambda+\rho_n$ as the n,n term. If this determinant is transformed to an upper triangular form, the value of the determinant will be simply the product of the diagonal terms. Let N_j and D_j, respectively, be the numerator and the denominator of the transformed j-th diagonal term, then

$$\begin{array}{llll} \cdots \frac{N_j}{D_j} & \rho_j & \cdots & \text{[transformed j-th row]} \\ \cdots \rho_j & \lambda & \rho_{j+1} & \text{[original (j+1)-st row]} . \end{array} \tag{VI-15}$$

The j-th row is multiplied by K_j, and the product is added to the (j+1)-st row. K_j is chosen so that the term to the left of the diagonal term becomes zero on transformation. Thus,

$$\rho_j + K_j \left(\frac{N_j}{D_j}\right) = 0$$

or

$$K_j = \frac{-\rho_j D_j}{N_j} . \tag{VI-16}$$

The transformed diagonal term becomes

$$\begin{aligned} \frac{N_{j+1}}{D_{j+1}} &= \lambda + K_j \rho_j \\ &= \lambda - \frac{\rho_j^2 D_j}{N_j} \\ &= \frac{\lambda N_j - \rho_j^2 D_j}{N_j} \end{aligned} \tag{VI-17}$$

Thus,

(VI-18) $$N_{j+1} = \lambda N_j - \rho_j^2 D_j$$

and

(VI-19) $$D_{j+1} = N_j ,$$

which yield

(VI-20) $$N_{j+1} = \lambda N_j - \rho_j^2 N_{j-1}$$

or

(VI-21) $$N_j = \lambda N_{j-1} - \rho_{j-1}^2 N_{j-2} .$$

For the final diagonal term we have

(VI-22) $$\begin{aligned} \frac{N_n}{D_n} &= \lambda + \rho_n + K_{n-1}\, \rho_{n-1} \\ &= \lambda + \rho_n - \frac{\rho_{n-1}^2\, D_{n-1}}{N_{n-1}} \\ &= \frac{(\lambda+\rho_n)N_{n-1} - \rho_{n-1}^2\, N_{n-2}}{N_{n-1}} \end{aligned}$$

and

(VI-23) $$N_n = (\lambda+\rho_n)N_{n-1} - \rho_{n-1}^2\, N_{n-2} .$$

Furthermore,

(VI-24) $$N_1 = \lambda ,$$

and

(VI-25) $$N_0 = 1 .$$

D. THE EIGENVECTORS

The molecular orbitals, $|\psi_k\rangle$, are taken as linear combinations of the atomic orbitals, $|u_i\rangle$. Thus,

$$(A\text{-}25) \qquad |\psi_k\rangle = \sum_{i=1}^{n} \bar{z}_{ik} |u_i\rangle \;,$$

where the bar over the coefficients, z_{ik}, is used to indicate that the molecular orbitals are not normalized. The secular determinant, (IV-45), comes from (A-52) rewritten as

$$(VI\text{-}26) \qquad (\lambda_k \, \delta_{ij} + \rho_{ij}) |\bar{z}_{ik}\rangle \;,$$

where, for example, $\rho_{12} = \rho_1$ in (IV-45), and δ_{ij} is the Kronecker delta. Equation (VI-26) represents n simulataneous linear equations. For the polyenes the first equation is

$$(VI\text{-}27) \qquad \lambda_k \, \bar{z}_{1k} + \rho_1 \, \bar{z}_{2k} = 0 \;;$$

the n-th is

$$(VI\text{-}28) \qquad \rho_{n-1} \, \bar{z}_{n-1,k} + (\lambda_k + \rho_n) \, \bar{z}_{n,k} = 0 \;;$$

and the remaining n-2 equations can be represented by

$$(VI\text{-}29) \qquad \rho(j) \, \bar{z}(j,k) + \lambda(k) \, \bar{z}(j+1,k) + \rho(j+1) \, \bar{z}(j+2,k) = 0 \;, \qquad j = 1, \ldots, n-2 \;,$$

where the format has been changed to permit somewhat easier reading.

From (VI-27) we obtain

$$\bar{z}(2,k) = \frac{-\lambda(k)\ \bar{z}(1,k)}{\rho(1)}\ , \tag{VI-30}$$

and from (VI-29) we obtain

$$\bar{z}(j+2,k) = \frac{-\rho(j)\ \bar{z}(j,k) - \lambda(k)\ \bar{z}(j+1,k)}{\rho(j+1)}\ , \qquad j = 1, \ldots, n-2\ . \tag{VI-31}$$

For $j = 1$, (VI-31) becomes

$$\begin{aligned} \bar{z}(3,k) &= \frac{-\rho(1)\ \bar{z}(1,k) - \lambda(k)\ \bar{z}(2,k)}{\rho(2)} \\ &= \frac{-\rho(1)\ \bar{z}(1,k) + [\lambda(k)^2\ \bar{z}(1,k)/\rho(1)]}{\rho(2)} \qquad \text{[by (VI-30)]}\ . \end{aligned} \tag{VI-32}$$

Thus, we see that all of the $\bar{z}(j,k)$'s are proportional to $\bar{z}(1,k)$ and that (VI-28) is not used. Since (VI-28) is not used, we can use (VI-31) to obtain all of the $\bar{z}(j,k)$'s provided that we change the signs of the $\lambda(k)$'s for $k \geq n+1-p$. Furthermore, with no loss of generality we can assign $\bar{z}(1,k)$ the value

$$\bar{z}(1,k) = 1.0\ . \tag{VI-33}$$

Using (VI-7) we obtain

$$\left.\begin{aligned} &\text{(VI-34)} \qquad \bar{z}(2,k) = \frac{\mu(k)}{\rho_1} \\ &\text{(VI-35)} \qquad \bar{z}(j+2,k) = \frac{-\rho(j)\ \bar{z}(j,k) + \mu(k)\ \bar{z}(j+1,k)}{\rho(j+1)} \end{aligned}\right\}\ k = 1,\ \ldots,\ n-p\ ,$$

and

$$\left.\begin{aligned} &\text{(VI-36)} \qquad \bar{z}(2,k) = \frac{-\mu(k)}{\rho_1} \\ &\text{(VI-37)} \qquad \bar{z}(j+2,k) = \frac{-\rho(j)\ \bar{z}(j,k) - \mu(k)\ \bar{z}(j+1,k)}{\rho(j+1)} \end{aligned}\right\}\ k = n+1-p,\ \ldots,\ n\ .$$

The normalized values of the $z(j,k)$'s are given by

$$\text{(VI-38)} \qquad z(j,k) = N(k)\ \bar{z}(j,k)\ ,$$

where

$$\text{(VI-39)} \qquad N(k) = \left\{ \sum_{j=1}^{n} \bar{z}(j,k)^2 + 2 \sum_{j=1}^{n-1} \bar{z}(j,k)\ \bar{z}(j+1,k)\ \$(j,j+1) \right\}^{-1/2}\ ,$$

where

$$\begin{aligned} \text{(VI-40)} \qquad \$(j,j+1) &= \$\ \rho(j,j+1) \\ &= \$\rho(j) \\ &= 0.2455\ \rho(j)\ . \end{aligned}$$

For the polyenes with symmetry factoring (VI-39) must be modified to

$$\text{(VI-41)} \qquad N(k) = \left\{ 2 \sum_{j=1}^{n} \bar{z}(j,k)^2 + 0.982 \sum_{j=1}^{n-1} \bar{z}(j,k)\, \bar{z}(j+1,k)\, \rho(j) \pm 0.2455\, \bar{z}(n,k)^2\, \rho(n) \right\}^{-1/2} ,$$

where the factors of two have been introduced because (IV-45) represents only half of the molecule. The last term is the result of the interaction between the two halves of the molecule. The plus sign is used when $k = 1, \ldots, n-p$, and the minus sign is used when $k = n+1-p, \ldots, n$. It should be recalled that n is only half the number of carbon atoms [cf. (VI-4)]. Because of symmetry

$$\text{(VI-42)} \qquad \bar{z}(j,k) = \pm\, \bar{z}(m+1-j,\, k) \quad ,$$

where the plus sign is used for the symmetric cases $[k = 1, \ldots, n-p]$, and the minus sign is used for the antisymmetric cases $[k = n+1-p, \ldots, n]$. The sign factor of (VI-42) plays a role only in the last term of (VI-41).

E. EXAMPLES OF ρ-POLYNOMIALS

1. $n = 2$

By (VI-23)

$$\text{(VI-43)} \qquad \begin{aligned} N(n = 2) &= (\lambda+\rho_2)N_1 - \rho_1^2 N_0 \\ &= (\lambda+\rho_2)\lambda - \rho_1^2 \qquad \text{[by (VI-24) and (VI-25)]} \\ &= \lambda^2 + \rho_2\lambda - \rho_1^2 \quad . \end{aligned}$$

Thus,

(VI-44) $$a_1 = \rho_n ,$$

and

(VI-45) $$a_2 = -\rho_{n-1}^2 .$$

2. n = 3

By (VI-23) and (VI-21)

(VI-46) $$\begin{aligned} N(n = 3) &= (\lambda+\rho_3)N_2 - \rho_2^2 N_1 \\ &= (\lambda+\rho_3)\ (\lambda N_1 - \rho_1^2 N_0) - \rho_2^2 N_1 \\ &= (\lambda+\rho_3)\ (\lambda^3-\rho_1^2) - \rho_2^2\lambda \\ &= \lambda^3+\rho_3\lambda^2 - (\rho_1^2+\rho_2^2)\lambda - \rho_3\rho_1^2 \end{aligned}$$

Thus,

(VI-47) $$a_1 = \rho_n ,$$

(VI-48) $$a_2 = -(\rho_{n-1}^2 + \rho_{n-2}^2)$$

and

(VI-49) $$a_3 = -\rho_n\ \rho_{n-2}^2$$

The ρ's in terms of the a's are

(VI-50) $$\rho_n = a_1 ,$$

(VI-51) $$\rho_{n-2}^2 = -a_3/\rho_n$$

$$= -a_3/a_1$$

and

(VI-52) $$\rho_{n-1}^2 + \rho_{n-2}^2 = -a_2$$

or

(VI-53) $$\rho_{n-1}^2 = -a_2 - \rho_{n-2}^2$$

$$= -a_2 + a_3/a_1 .$$

3. $n = 4$

By (VI-23) and (VI-21) with the recognition that $N_2 = \lambda^2-\rho_1^2$,

(VI-54) $$N(n - 4) = (\lambda+\rho_4)N_3 - \rho_3^2N_2$$

$$= (\lambda+\rho_4)\ (\lambda N_2-\rho_2^2N_1) - \rho_3^2(\lambda^2-\rho_1^2)$$

$$= (\lambda+\rho_4)\ (\lambda\{\lambda^2-\rho_1^2\} - \rho_1^2\lambda) - \rho_3^2(\lambda^2-\rho_1^2)$$

$$= (\lambda+\rho_4)\ (\lambda^3 - \{\rho_1^2+\rho_2^2\}\lambda) - \rho_3^2(\lambda^2-\rho_1^2)$$

$$= \lambda^4 + \rho_4\lambda^3 - (\rho_1^2+\rho_2^2+\rho_3^2)\lambda^2 - \rho_4(\rho_1^2+\rho_2^2)\lambda + \rho_3^2\rho_1^2 .$$

Thus,

(VI-55) $$a_1 = \rho_n ,$$

(VI-56) $$a_2 = -(\rho^2_{n-1} + \rho^2_{n-2} + \rho^2_{n-3}) ,$$

(VI-57) $$a_3 = -\rho_n(\rho^2_{n-2} + \rho^2_{n-3}) ,$$

and

(VI-58) $$a_4 = \rho^2_{n-1}\ \rho^2_{n-3} .$$

The ρ's in terms of the a's are obtained by

(VI-59) $$\rho_n = a_1 ,$$

(VI-60) $$(\rho^2_{n-1} + \rho^2_{n-2} + \rho^2_{n-3}) = -a_2 \qquad \text{[by (VI-56)]} ,$$

(VI-61) $$(\rho^2_{n-2} + \rho^2_{n-3}) = -a_3/a_1 \qquad \text{[by (VI-55) and (VI-57)]} ,$$

(VI-62) $$\rho^2_{n-1} = -a_2 + a_3/a_1 ,$$

(VI-63) $$\rho^2_{n-3} = a_4/\rho^2_{n-1} \qquad \text{[by (VI-58) and (VI-62)]} ,$$

and

(VI-64) $$\begin{aligned}\rho^2_{n-2} &= -a_3/a_1 - \rho^2_{n-3} \\ &= -a_3/a_1 - a_4/\rho^2_{n-1} .\end{aligned}$$

4. SUMMARY OF $a(i,n)$'s AS FUNCTIONS OF $\rho(n-j)$'s

The above examples for $n = 2,3,4$ demonstrate the algebraic manipulations which are required to obtain a_i's as functions of the ρ_j's and vice versa. The only purpose which can be served by looking at further examples is the determination of patterns in the relations. Instead of deriving more examples here we shall list the results for $n = 10$. As an aid to the attaining of results later we shall write $a_i(n = \ )$ as $a\,(i,n)$. Thus, $a_5\,(n = 10)$ will be written as $a(5,10)$.

$$a(1,10) = \rho(n) \tag{VI-65}$$

$$a(2,10) = -\sum_{j=1}^{n-1} \rho(n-j)^2 , \tag{VI-66}$$

$$a(3,10) = -a(1,10) \sum_{j=2}^{n-1} \rho(n-j)^2 , \tag{VI-67}$$

$$a(4,10) = \sum_{j=1}^{n-3} \rho(n-j)^2 \sum_{k=j+2}^{n-1} \rho(n-k)^2 , \tag{VI-68}$$

$$a(5,10) = a(1,10) \sum_{j=2}^{n-3} \rho(n-j)^2 \sum_{k=j+2}^{n-1} \rho(n-k)^2 , \tag{VI-69}$$

$$a(6,10) = -\sum_{j=1}^{n-5} \rho(n-j)^2 \sum_{k=j+2}^{n-3} \rho(n-k)^2 \sum_{\ell=k+2}^{n-1} \rho(n-\ell)^2 , \tag{VI-70}$$

$$a(7,10) = -a(1,10) \sum_{j=2}^{n-5} \rho(n-j)^2 \sum_{k=j+2}^{n-3} \rho(n-k)^2 \sum_{\ell=k+2}^{n-1} \rho(n-\ell)^2 , \tag{VI-71}$$

$$a(8,10) = \sum_{n=1}^{n-7} \rho(n-j)^2 \sum_{k=j+2}^{n-5} \rho(n-k)^2 \sum_{\ell=k+2}^{n-3} \rho(n-\ell)^2 \sum_{m=\ell+2}^{n-1} \ell(n-m)^2 , \tag{VI-72}$$

$$\text{(VI-73)} \qquad a(9,10) = a(1,10) \sum_{j=2}^{n-7} \rho(n-j)^2 \sum_{k=j+2}^{n-5} \rho(n-k)^2 \sum_{\ell=k+2}^{n-3} (n-\ell)^2 \sum_{m=\ell+2}^{n-1} \rho(n-m)^2$$

and

$$\text{(VI-74)} \qquad a(10,10) = - \sum_{j=1}^{n-9} \rho(n-j)^2 \sum_{k=j+2}^{n-7} \rho(n-k)^2 \sum_{\ell=k+2}^{n-5} \rho(n-\ell)^2 \sum_{m=\ell+2}^{n-3} \rho(n-m)^2 \sum_{p=m+2}^{n-1} \rho(n-p)^2$$

It will be convenient for use to introduce a symbol from Fortran at this time. If i is an <u>integer</u> and is <u>even</u>, MOD$(i,2) = 0$. If i is an <u>integer</u> and is <u>odd</u>, MOD$(i,2) = 1$. For MOD$(i,2) = 1$, $a(i,n)$ has a factor of $a(1,n)$, and for the MOD$(i,2) = 1$ sequence the sign alternates starting with minus for $i = 3$. If we take

$$\text{(VI-75)} \qquad i = 2\alpha + 1 \ ,$$

we can write the MOD$(i,2) = 1$ sequence starting with $i = 3$ in the general form

$$\text{(VI-76)} \qquad a(i,n) = (-1)^{\alpha} a(1,n) \sum_{j_1=2}^{n+2-i} \rho(n-j_1)^2 \sum_{j_2=j_1+2}^{n+4-i} \rho(n-j_2)^2 \cdots \sum_{j_p=j_{p-1}+2}^{n-1} \rho(n-j_p)^2 \ , \qquad \text{MOD}(i,2) = 1 \ .$$

Similarly, for MOD$(i,2) = 0$,

$$\text{(VI-77)} \qquad i = 2\beta \ ,$$

and

$$\text{(VI-78)} \qquad a(i,n) = (-1) \sum_{j_1=1}^{n+1-i} \rho(n-j_1)^2 \sum_{j_2=j_1+2}^{n+3-i} \rho(n-j_2)^2 \cdots \sum_{j_q=j_{q-1}+2}^{n-1} \rho(n-j_q)^2 , \qquad \text{MOD}(i,2) = 0 .$$

F. GENERATOR FUNCTIONS FOR $\rho(n-j)$'s AS FUNCTIONS OF $a(i,n)$'s

1. INTRODUCTION

We shall now introduce two sets of abbreviations which will expedite the writing of the mathematics and make the reading of it less of a chore. The expressions

$$a(\alpha,n)/\rho(n-\beta)^2 \ \rho(n-\gamma)^2 \ \rho(n-\delta)^2$$

and

$$a(\alpha,n)/\rho(n) \ \rho(n-\beta)^2 \ \rho(n-\gamma)^2 \ \rho(n-\delta)^2$$

will be written as $(\alpha/\beta,\gamma,\ \delta)$ and $(\alpha/0,\ \beta,\ \gamma,\ \delta)$, respectively. Furthermore, the instruction

$$[(x) - (y), \div z]$$

shall be taken to mean 'subtract equation (y) from equation (x) and divide the <u>difference</u> by the term z'. Thus, for $n = 10$,

$$(\text{VI-79})\quad \sum_{j=1}^{9} \rho(n-j)^2 = -(2) \qquad [(\text{VI-66}) \div -1]\ ,$$

$$(\text{VI-80})\quad \sum_{j=2}^{9} \rho(n-j)^2 = -(3/0) \qquad [(\text{VI-67}) \div -a(1,10)]\ ,$$

$$(\text{VI-81})\quad \rho(n-1)^2 = -(2) + (3/0) \qquad [(\text{VI-79}) - (\text{VI-80})]\ ,$$

$$(\text{VI-82})\quad \sum_{j=2}^{7} \rho(n-j)^2 \sum_{k=j+2}^{9} \rho(n-k)^2 = (5/0) \qquad [(\text{VI-69}) \div a(1,10)]\ ,$$

$$(\text{VI-83})\quad \sum_{j=3}^{9} \rho(n-j)^2 = (4/1) - (5/0,1) \qquad [(\text{VI-68}) - (\text{VI-82})\ , \div (n-1)^2]\ ,$$

$$(\text{VI-84})\quad \rho(n-2)^2 = -(3/0) - (4/1) + (5/0,1) \qquad [(\text{VI-80}) - (\text{VI-83})]\ ,$$

$$(\text{VI-85})\quad \sum_{j=1}^{5} \rho(n-j)^2 \sum_{k=j+2}^{7} \rho(n-k)^2 \sum_{\ell=k+2}^{9} \rho(n-\ell)^2 = -(6) \qquad [(\text{VI-70}) \div -1]\ ,$$

$$(\text{VI-86})\quad \sum_{j=2}^{5} \rho(n-j)^2 \sum_{k=j+2}^{7} \rho(n-k)^2 \sum_{\ell=k+2}^{9} \rho(n-\ell)^2 = -(7/0) \qquad [(\text{VI-71}) \div -a(1,10)]\ ,$$

$$(\text{VI-87})\quad \sum_{j=3}^{7} \rho(n-j)^2 \sum_{k=j+2}^{9} \rho(n-k)^2 = -(6/1) + (7/0,1) \qquad [(\text{VI-85}) - (\text{VI-86}), \div\rho(n-1)^2]\ ,$$

$$(\text{VI-88})\quad \sum_{j=4}^{9} \rho(n-j)^2 = (5/0,2) + (6/1,2) - (7,/0,1,2) \qquad [(\text{VI-82}) - (\text{VI-87}), \div\rho(n-2)^2]\ ,$$

$$(\text{VI-89})\quad \rho(n-3)^2 = (4/1) - (5/10,1) - (5/0,2) - (6/1,2) + (7/0,1,2) \qquad [(\text{VI-83}) - (\text{VI-88})]\ ,$$

$$(\text{VI-90})\quad \sum_{j=2}^{3} \rho(n-j)^2 \sum_{k=j+2}^{5} \rho(n-k)^2 \sum_{\ell=k+2}^{7} \rho(n-\ell)^2 \sum_{m=\ell+2}^{9} \rho(n-m)^2 = (9/0) \qquad [(\text{VI-73}) \div a(1,10)]\ ,$$

$$\text{(VI-91)}\quad \sum_{j=3}^{5} \rho(n-j)^2 \sum_{k=j+2}^{7} \rho(n-k)^2 \sum_{\ell=k+2}^{9} \rho(n-\ell)^2 = (8/1)-(9/0,1)$$

$$[(\text{VI-72}) - (\text{VI-90}),\ \rho(n-1)^2]\ ,$$

$$\text{(VI-92)}\quad \sum_{j=4}^{7} \rho(n-j)^2 \sum_{k=j+2}^{9} \rho(n-k)^2 = -(7/0,2) - (8/1,2) + (9/0,1,2)$$

$$[(\text{VI-86}) - (\text{VI-91}),\ \rho(n-2)^2]\ ,$$

$$\text{(VI-93)}\quad \sum_{j=5}^{9} \rho(n-j)^2 = -(6/1,3) + (7/0,1,3) + (7/0,2,3) + (8/1,2,3) - (9/0,1,2,3)$$

$$[(\text{VI-87}) - (\text{VI-92}), \div \rho(n-3)^2]\ ,$$

$$\text{(VI-94)}\quad \rho(n-4)^2 = (5/0,2) + (6/1,2) + (6/1,3) - (7/0,1,2) - (7/0,1,3)$$

$$- (7/0,2,3) - (8/1,2,3) + (9/0,1,2,3)$$

$$[(\text{VI-88}) - (\text{VI-93})]\ ,$$

$$\text{(VI-95)}\quad \sum_{j=3}^{3} \rho(n-j)^2 \sum_{k=j+2}^{5} \rho(n-k)^2 \sum_{\ell=k+2}^{7} \rho(n-\ell)^2 \sum_{m=\ell+2}^{9} \rho(n-m)^2 = -(10/1)$$

$$[(\text{VI-74}) \div \rho(n-1)^2]\ ,$$

$$\text{(VI-96)}\quad \sum_{j=4}^{5} \rho(n-j)^2 \sum_{k=j+2}^{7} \rho(n-k)^2 \sum_{\ell=k+2}^{9} \rho(n-\ell)^2 = (9/0,2) + (10/1,2)$$

$$[(\text{VI-90}) - (\text{VI-95}), \div \rho(n-2)^2]\ ,$$

$$\text{(VI-97)}\quad \sum_{j=5}^{7} \rho(n-j)^2 \sum_{k=j+2}^{9} \rho(n-k)^2 = (8/1,3) - (9/0,1,3) - (9/0,2,3)$$

$$- (10/1,2,3) \quad [(\text{VI-91}) - (\text{VI-96}), \div \rho(n-3)^2]\ ,$$

$$\text{(VI-98)}\quad \sum_{j=6}^{9} \rho(n-j)^2 = -(7/0,2,4) - (8/1,2,4) - (8/1,3,4)$$

$$+(9/0,1,2,4) + (9/0,1,3,4) + (9/0,2,3,4)$$

$$+ (10/1,2,3,4) \qquad [(\text{VI-92}) - (\text{VI-97}), \div \rho(n-4)^2] ,$$

$$\text{(VI-99)}\quad \rho(n-5)^2 = - (6/1,3) + (7/0,1,3) + (7/0,2,3) + (7/0,2,4)$$

$$+ (8/1,2,3) + (8/1,2,4) + (8/1,3,4)$$

$$- (9/0,1,2,3) - (9/0,1,2,4) - (9/0,1,3,4) - (9/0,2,3,4)$$

$$- (10/1,2,3,4) \qquad [(\text{VI-93}) - (\text{VI-98})] ,$$

$$\text{(VI-100)}\quad \sum_{j=5}^{5} \rho(n-j)^2 \sum_{k=j+2}^{7} \rho(n-k)^2 \sum_{\ell=k+2}^{9} \rho(n-\ell)^2 = -(10/1,3)$$

$$[(\text{VI-95}) \div \rho(n-3)^2] ,$$

$$\text{(VI-101)}\quad \sum_{j=6}^{7} \rho(n-j)^2 \sum_{k=j+2}^{9} \rho(n-k)^2 = (9/0,2,4) + (10/1,2,4) + (10/1,3,4)$$

$$[(\text{VI-96}) - (\text{VI-100}), \div \rho(n-4)^2] ,$$

$$\text{(VI-102)}\quad \sum_{j=7}^{9} \rho(n-j)^2 = (8/1,3,5) - (9/0,1,3,5) - (9/0,2,3,5) - (9/0,2,4,5)$$

$$- (10/1,2,3,5) - (10/12,4,5) - (10/1,3,4,5)$$

$$[(\text{VI-97}) - (\text{VI-101}), \div \rho(n-5)^2] ,$$

$$\begin{aligned}\text{(VI-103)}\quad \rho(n-6)^2 = &-(7/0,2,4) - (8/1,2,4) - (8/1,3,4) - (8/1,3,5)\\ &+ (9/0,1,2,4) + (9/0,1,3,4) + (9/0,2,3,4) + (9/0,1,3,5)\\ &+ (9/0,2,3,5) + (9/0,2,4,5) + (10/1,2,3,4) + (10/1,2,3,5)\\ &+ (10/1,2,4,5) + (10/1,3,4,5) \qquad [(\text{VI-99}) - (\text{VI-102})]\ ,\end{aligned}$$

$$\text{(VI-104)}\quad \sum_{j=7}^{7} \rho(n-j)^2 \sum_{k=j+2}^{9} \rho(n-k)^2 = -(10/1,3,5) \qquad [(\text{VI-100}) \div \rho(n-5)^2]\ ,$$

$$\begin{aligned}\text{(VI-105)}\quad \sum_{8}^{9} \rho(n-j)^2 = &\ (9/0,2,4,6) + (10/1,2,4,6) + (10/1,3,4,6)\\ &+ (10/1,3,5,6) \qquad [(\text{VI-101}) - (\text{VI-104}), \div \rho(n-6)^2]\ ,\end{aligned}$$

$$\begin{aligned}\text{(VI-106)}\quad \rho(n-7)^2 = &\ (8/1,3,5) - (9/0,1,3,5) - (9/0,2,3,5) - (9/0,2,4,5)\\ &- (9/0,2,4,6) - (10/1,2,3,5) - (10/1,2,4,5)\\ &- (10/1,3,4,5) - (10/1,2,4,6) - (10/1,3,4,6)\\ &- (10/1,3,5,6) \qquad [(\text{VI-102}) - (\text{VI-105})]\ ,\end{aligned}$$

$$\text{(VI-107)}\quad \rho(n-9)^2 = -(10/1,3,5,7) \qquad [(\text{VI-104}) \div \rho(n-7)^2]\ ,$$

and

$$\begin{aligned}\text{(VI-108)}\quad \rho(n-8)^2 = &\ (9/0,2,4,6) + (10/1,2,4,6) + (10/1,3,4,6)\\ &+ (10/1,3,5,6) + (10/1,3,5,7) \qquad [(\text{VI-105}) - (\text{VI-107})]\ .\end{aligned}$$

2. SIGNS

For the present we shall consider only the presence or absence of the various $a(i,n)$'s and, when present, their signs relative to a specific $\rho(n-j)^2$ [or $\rho(n)$ itself] for $n = 10$. Thus,

$$
\begin{array}{llllll}
n & +a_1 & & & & \\
n-1 & -a_2 & +a_3 & & & \\
n-2 & -a_3 & -a_4 & +a_5 & & \\
n-3 & +a_4 & -a_5 & -a_6 & +a_7 & \\
n-4 & +a_5 & +a_6 & -a_7 & -a_8 & +a_9 \\
n-5 & -a_6 & +a_7 & +a_8 & -a_9 & -a_{10} \\
n-6 & -a_7 & -a_8 & +a_9 & +a_{10} & \\
n-7 & +a_8 & -a_9 & -a_{10} & & \\
n-8 & +a_9 & +a_{10} & & & \\
n-9 & -a_{10} & & & &
\end{array}
\tag{VI-109}
$$

Three trends can be seen easily from (VI-109). For each $\rho(n-j)$ the lowest value of i is $j+1$. The highest value of i is $2j+1$ or n, whichever is smaller. The vertical sign pattern starting from the top is $+ - - + + - - + +$ etc., where after the first singleton $+$ all signs are in pairs.

We shall consider first the cases for which MOD(i,2) = 1. The first portion of the '(j,i) sign' array is

$$\text{(VI-110)}\qquad \begin{array}{ccccccc}
(0,1)+ & & & & & & \\
 & (1,3)+ & & & & & \\
(2,3)- & & (2,5)+ & & & & \\
 & (3,5)- & & (3,7)+ & & & \\
(4,5)+ & & (4,7)- & & (4,9)+ & & \\
 & (5,7)+ & & (5,9)- & & (5,11)+ & \\
(6,7)- & & (6,9)+ & & (6,11)- & & (6,13)+
\end{array}$$

For a constant i a $\delta_j = 1$ causes a change of sign. For a constant j a $\delta_i = 2$ causes a change of sign. Thus, the sign factor in terms of the δ's is

$$\text{(VI-111)}\qquad (-1)^{\delta_j}\,(-1)^{\delta_i/2}$$

The lowest value of j is 0, and the lowest value of i is 1. Furthermore, the sign of (0,1) is +. Thus, the MOD(i,2) = 1 sign factor is

$$\text{(VI-112)}\qquad (-1)^{j}\,(-1)^{(i-1)/2} = (-1)^{(2j+i-1)/2}\,, \quad \mathrm{MOD}(i,2) = 1$$

For MOD(i,2) = 0 the first portion of the '(j,i) sign' array is

(VI-113)

$$\begin{array}{lllll}
(1,2)- & & & & \\
 & (2,4)- & & & \\
(3,4)+ & & (3,6)- & & \\
 & (4,6)+ & & (4,8)- & \\
(5,6)- & & (5,8)+ & & (5,10)- \\
 & (6,8)- & & (6,10)+ & \\
(7,8)+ & & (7,10)- & & \\
 & (8,10)+ & & & \\
(9,10)- & & & &
\end{array}$$

For a constant i and $\delta_j = 1$ causes a change of sign. For a constant j a $\delta_i = 2$ causes a change of sign. Furthermore, the sign of $(1,2)$ is $-$. Thus, the sign factor is

$$(-1)\ (-1)^j\ (-1)^{i/2} = (-1)^{(2j+i+2)/2}, \qquad \mathrm{MOD}(i,2) = 0 . \tag{VI-114}$$

3. GENERAL FORM OF THE GENERATOR FUNCTION

If $\mathrm{MOD}(i,2) = 1$, we may take

$$i = 2k+1 , \tag{VI-115}$$

where the k's are a sequence of cardinal numbers. The first and last members will be determined later. If $\mathrm{MOD}(i,2) = 0$, we may take

(VI-116) $$i = 2\ell ,$$

where again the ℓ's are a sequence of cardinal numbers. The general form for $\rho(n-j)^2$ may now be written as

(VI-117) $$\rho(n-j)^2 = \sum_k (-1)^j (-1)^k a_1^{-1} K(k) a(2k+1) + \sum_\ell (-1) (-1)^j (-1)^\ell L(\ell) a(2\ell) = (-1)^j [\sum_k (-1)^k K(k) a(2k+1)/a(1) - \sum_\ell (-1)^\ell L(\ell) a(2\ell)] ,$$

where $K(k)$ and $L(\ell)$ are products of the type $\rho(n-\alpha)^{-2} \rho(n-\beta)^2 \ldots$.

Following (VI-109) it was noted that the boundary conditions on i are

(VI-118) $$j+1 \leq i \leq 2j+1$$

or

(VI-119) $$j+1 \leq i \leq n ,$$

depending upon whether $n < 2j+1$ or $2j+1 < n$.

We may now distinguish two cases, MOD(j,2) = 1 and MOD(j,2) = 0. For MOD(j,2) = 0, j+1 is odd, and the lowest possible value of i is odd. Thus, (VI-115) is used, and

(VI-120) $$2k(\min) + 1 = j+1$$

or

(VI-121) $$k(\min) = j/2 \;, \qquad \mathrm{MOD}(j,2) = 0 \;,$$

and

(VI-122) $$2\ell(\min) = j+2$$

or

(VI-123) $$\ell(\min) = (j+2)/2 \;, \qquad \mathrm{MOD}(j,2) = 0 \;.$$

For MOD(j,2) = 1, MOD(j+1,2) = 0. Thus, (VI-116) is used, and

(VI-124) $$2\ell(\min) = j+1$$

or

(VI-125) $$\ell(\min) = (j+1)/2 \;, \qquad \mathrm{MOD}(j,2) = 1 \;,$$

and

(VI-126) $$2k(\min) + 1 = j+2$$

or

(VI-127) $$k(\text{min}) = (j+1)/2\ , \qquad \text{MOD}(j,2) = 1$$

These minimum value results are summarized by

(VI-128)

	$\text{MOD}(j,2) = 0$	$\text{MOD}(j,2) = 1$
$k(\text{min})$	$j/2$	$(j+1)/2$
$\ell(\text{min})$	$(j+2)/2$	$(j+1)/2$

We now define two new functions

(VI-129) $$2r = j+2 - \text{MOD}(j,2)$$

and

(VI-130) $$2s = j + \text{MOD}(j,2)$$

Thus, for all j

(VI-131) $$k(\text{min}) = s$$

and

(VI-132) $$\ell(\text{min}) = r$$

From (VI-109) it is found that (VI-118) applies if

(VI-133) $$j \leq \mathrm{INT}(\frac{n}{2}) - 1 \quad ,$$

where INT(z) is 'round down' integer related to z. For example, INT(+ 2.1) = +2, INT(+ 2.0) = +2 and INT(- 3.5) = -4. The function p was introduced in (VI-6). It can be defined by

(VI-134) $$p = \mathrm{INT}(\frac{n}{2}) \quad .$$

Equation (VI-119) applies if

(VI-135 $$j \geq p \quad .$$

For (VI-118) the upper value of i is always odd. Thus,

(VI-136) $$2k(\max) + 1 = 2j+1$$

or

(VI-137) $$k(\max) = j \quad , \qquad 2j+1 \leq n$$

and

(VI-138) $$2\ell(\max) = 2j$$

or

(VI-139) $$\ell(\max) = j \quad , \qquad 2j+1 \leq n \quad .$$

For (VI-119), if $MOD(n,2) = 0$,

(VI-140) $$2\ell(max) = n$$

or

(VI-141) $$\ell(max) = n/2$$

$$= p , \qquad MOD(n,2) = 0 ,$$

and

(VI-142) $$2k(max) + 1 = n-1$$

or

(VI-143) $$k(max) = (n-2)/2$$

$$= p-1$$

$$= p + MOD(n,2) - 1 \qquad [\text{since } MOD(n,2) = 0] .$$

For $MOD(n,2) = 1$,

(VI-144) $$2k(max) + 1 = n$$

or

(VI-145)
$$\begin{aligned} k(\max) &= (n-1)/2 \\ &= p \\ &= p + \mathrm{MOD}(n,2) - 1 \qquad [\text{since } \mathrm{MOD}(n,2) = 1] , \end{aligned}$$

and

(IV-146)
$$2\ell(\max) = n-1$$

or

(VI-147)
$$\begin{aligned} \ell(\max) &= (n-1)/2 \\ &= p , \qquad \mathrm{MOD}(n,2) = 1 . \end{aligned}$$

If we define

(VI-148)
$$q = p + \mathrm{MOD}(n,2) - 1 ,$$

the bounds of k and ℓ may be written as

(VI-149)
$$\begin{aligned} k &= s, \ldots, j; \qquad 2j+1 \le n \\ &= s, \ldots, q; \qquad 2j+1 \ge n , \end{aligned}$$

and

(IV-150)
$$\begin{aligned} \ell &= r, \ldots, j; \qquad 2j+1 \le n \\ &= r, \ldots, p; \qquad 2j+1 \ge n . \end{aligned}$$

4. GENERATOR FUNCTION FOR K(k)

The symbol (4,3) 1,2 is to be taken to mean that for $j = 4$ and $k = 3$ $(i = 7)$, K(k) has the term $\rho(n-1)^{-2}\,\rho(n-2)^{-2}$ in it. With this symbolism the data of SECTION VI.F.1 for MOD(i,2) = 1 and $n = 10$ are represented by

(VI-151)

(2,2)1	(3,2)1 2	(4,2)2		
(3,3)1,2	(4,3)1,2 1,3 2,3	(5,3)1,3 2,3 2,4	(6,3)2,4	
(4,4)1,2,3	(5,4)1,2,3 1,2,4 1,3,4 2,3,4	(6,4)1,2,4 1,3,4 2,3,4 1,3,5 2,3,5 2,4,5	(7,4)1,3,5 2,3,5 2,4,5 2,4,6	(8,4) 2,4,

The pattern of (VI-151) may be represented by

(VI-152)
$$K(j,k) = K(j-2, k-1)/[\rho(n+2-j)]^2 + K(j-1, k-1)/[\rho(n+1-j)]^2 ,$$

with the boundary requirements

(VI-153) $$K(j,k) = 0 \,, \qquad k > j \quad \text{or} \quad j > 2k$$

and

(VI-154) $$K(1,1) = K(2,1) = 1 \quad .$$

The use of these rules will be demonstrated by a few examples,

(VI-155) $$\begin{aligned} K(2,2) &= K(0,1)[\rho(n)]^2 + K(1,1)/[\rho(n-1)]^2 \\ &= [\rho(n-1)]^{-2} \end{aligned}$$

since $K(0,1) = 0$ by (VI-153) $[1 > 0]$.

(VI-156) $$\begin{aligned} K(3,2) &= K(1,1)/[\rho(n-1)]^2 + K(2,1)/[\rho(n-2)]^2 \\ &= [\rho(n-1)]^{-2} + [\rho(n-2)]^{-2} \;. \end{aligned}$$

(VI-157) $$\begin{aligned} K(4,2) &= K(2,1)/[\rho(n-2)]^2 + K(3,1)/[\rho(n-3)]^2 \\ &= [\rho(n-2)]^2 \end{aligned}$$

since $K(3,1) = 0$ by (VI-153) $[3 > 2\cdot 1]$.

If MOD(j,2) = 0, (VI-153) translates to

(VI-158) $$j/2 \leq k \leq j \;.$$

If MOD(j,2) = 1, (VI-153) translates to

(VI-159) $$(j+1)/2 \leq k \leq j.$$

These results are the same as (VI-149) so no new requirements are introduced here.

5. GENERATOR FUNCTION FOR L(ℓ)

For MOD(i,2) = 0 and n = 10 the data of SECTION VI.F.1 are represented by

(VI-160)

(2,2)1	(3,2)1			
(3,3)1,2	(4,3)1,2 1,3	(5,3)1,3		
(4,4)1,2,3	(5,4)1,2,3 1,2,4 1,3,4	(6,4)1,2,4 1,3,4 1,3,5	(7,4)1,3,5	
(5,5)1,2,3,4	(6,5)1,2,3,4 1,2,3,5 1,2,4,5 1,3,4,5	(7,5)1,2,3,5 1,2,4,5 1,3,4,5 1,2,4,6 1,3,4,6	(8,5)1,2,4,6 1,3,4,6 1,3,5,6 1,3,5,7	(9,5)1,3,5,7

The pattern of (VI-160) may be represented by

(VI-161) $$L(j,\ell) = L(j-2,\ \ell-1)/[\rho(n+2-j)]^2 + L(j-1,\ \ell-1)/[\rho(n+1-j)]^2 \ ,$$

with the boundary requirements

(VI-162) $$L(j,\ell) = 0\ , \qquad \ell > j \quad \text{or} \quad j > 2\ell-1$$

and

(VI-163) $$L(1,1) = 1\ .$$

A few examples of these rules are

(VI-164) $$L(2,2) = L(0,1)/[\rho(n)]^2 + L(1,1)/[\rho(n-1)]^2$$
$$= [\rho(n-1)]^{-2}$$

since $L(0,1) = 0$ by (VI-162) $[1 > 0]$

(VI-165) $$L(3,2) = L(1,1)/[\rho(n-1)]^2 + L(2,1)/[\rho(n-2)]^2$$
$$= [\rho(n-1)]^2\ .$$

since $L(2,1) = 0$ by (VI-162) $[2 > 2\cdot 1-1]$.

(VI-166) $$L(3,3) = L(1,2)/[\rho(n-1)]^2 + L(2,2)/[\rho(n-2)]^2$$
$$= L(2,2)/[\rho(n-2)]^2$$
$$= [\rho(n-1)]^{-2}\ [\rho(n-2)]^{-2} \qquad \text{[by (VI-164)]}$$

since $L(1,2) = 0$ by (VI-162) $[2 > 1]$.

(VI-167) $$L(4,3) = L(2,2)/[\rho(n-2)]^2 + L(3,2)/[\rho(n-3)]^2$$

$$= [\rho(n-1)]^{-2}\,[\rho(n-2)]^{-2} + [\rho(n-1)]^{-2}\,[\rho(n-3)]^{-2}\ .$$

If $\mathrm{MOD}(j,2) = 1$, (VI-162) translates to

(VI-168) $$(j+1)/2 \leq \ell \leq j\ .$$

If $\mathrm{MOD}(j,2) = 0$, (VI-162) translates to

(VI-169) $$(j+2)/2 \leq \ell \leq j\ .$$

These results are the same as those of (VI-150) so no new requirements are introduced here.

We now have all of the necessary functions to apply EBL Theory to the polyenes.

VII. EBL THEORY RESULTS FRO POLYENES

By (IV-45) there are $2n-1$ bonds in a symmetric polyene. We have used the functions of SECTION VI in combination with a minimization program to calculate the minimum value of $\Delta E_T^{\dagger}$ [cf. (VI-8)], the values of λ_j and r_j for $n = 2, \ldots, 25$, $n = 50$ and $n = 100$. Because of the lack of sufficient funds for computer time, we were not able to continue the study to larger values of n. In TABLE VII-1 are listed the algebraically smallest value of λ_j (lowest filled energy level), the algebraically largest negative value of λ_j (highest filled energy level) and the equilibrium bond length of the central bond.

Several interesting trends are apparent. The value of λ_j for the lowest filled energy level is asymptotic to -1.965, or some value close to it. The value of λ_j for the highest filled energy level also appears to approach an asymptote, but it is not clear how much that value will differ from -0.069. If the central bond is a 'single' bond, the asymptotic value is 1.426×10^{-10} meters or some value close to it. If the central bond is a 'double' bond, the asymptotic value is 1.386×10^{-10} meters or some value close to it. In SECTION IV.G.1 we noted that the carbon-carbon bond lengths for ethene, benzene and ethylene are 1.536×10^{-10} meters, 1.397×10^{-10} meters and 1.334×10^{-10} meters, respectively. The average of the ethane and ethylene values is 1.435×10^{-10} meters. Thus, we see that the central 'single' bond length tends to a value somewhat smaller than the average of the single and double bond lengths, and that the central 'double' bond length tends to a value slightly shorter than the benzene value. Thus, while an

TABLE VII-1

EBL THEORY RESULTS

FOR POLYENES

n	λ_1	λ_n	r_n (in units of 10^{-10} meters)
2	-1.618	-0.737	1.467
3	-1.779	-0.556	1.359
4	-1.850	-0.450	1.451
5	-1.887	-0.380	1.369
6	-1.908	-0.330	1.443
7	-1.922	-0.293	1.375
8	-1.931	-0.265	1.438
9	-1.938	-0.242	1.378
10	-1.943	-0.223	1.435
11	-1.946	-0.208	1.380
12	-1.949	-0.195	1.433
13	-1.952	-0.184	1.382
14	-1.953	-0.174	1.432
15	-1.955	-0.166	1.383
16	-1.956	-0.158	1.431
17	-1.957	-0.151	1.384
18	-1.958	-0.146	1.430
19	-1.959	-0.141	1.385
20	-1.959	-0.136	1.429
21	-1.960	-0.132	1.386
22	-1.960	-0.128	1.429
23	-1.961	-0.124	1.386
24	-1.961	-0.121	1.428
25	-1.962	-0.118	1.386
50	-1.965	-0.083	1.426
100	-1.965	-0.069	1.426

equilization of the 'single' and 'double' bond lengths does not occur, neither is it true that there is no mixing. In the 'no mixing' model all 'single' bonds are the same length as that of butadiene (1.467×10^{-10} meters) and all 'double' bonds are the same length as those of butadiene (1.343×10^{-10} meters). For $n = 100$ there is a sort of 'no mixing' model after one is about 1/5-th of the way into the molecule (cf. TABLE VII-2). The bond lengths are, however, different from those of butadiene.

The 'no mixing' model of polyene used by Grant and Batra [58] predicts a 'band gap' of 1.2 eV. Since 1 eV is 1.602×10^{-19} Joules, their 'band gap' energy is 1.92×10^{-19} Joules$\cdot$electron^{-1}. By (IV-87) with $\$ = 0.2455$ the energy gap between the highest filled orbital and the lowest empty orbital for $n = 100$ is

(VII-1)
$$\Delta E(\text{band gap}) = -\gamma\left[\frac{0.069}{1 - 0.069(0.2455)} - \frac{-0.069}{1 + 0.069(0.2455)}\right]$$
$$= -\,1.38 \times 10^{-1}\,\gamma\,.$$

For the Grant and Batra value of $\Delta E(\text{band gap})$

(VII-2)
$$\gamma(\text{Grant and Batra}) = \frac{-\,1.92 \times 10^{-19}}{1.38 \times 10^{-1}}$$
$$= -1.39 \times 10^{-18}\ \text{Joules}\cdot\text{electron}^{-1}\,.$$

By (VI-1) and (VI-2)

TABLE VII-2

EQUILIBRIUM BOND LENGTHS FOR n = 100

(in units of 10^{-10} meters)

j	r_j	j	r_j	j	r_j	j	r_j
1	1.350	26	1.427	51	1.388	76	1.426
2	1.454	27	1.388	52	1.426	77	1.389
3	1.369	28	1.427	53	1.388	78	1.426
4	1.442	29	1.388	54	1.426	79	1.389
5	1.376	30	1.426	55	1.388	80	1.426
6	1.437	31	1.388	56	1.426	81	1.389
7	1.380	32	1.426	57	1.389	82	1.426
8	1.434	33	1.388	58	1.426	83	1.389
9	1.382	34	1.426	59	1.389	84	1.426
10	1.432	35	1.388	60	1.426	85	1.389
11	1.384	36	1.426	61	1.389	86	1.426
12	1.430	37	1.388	62	1.426	87	1.389
13	1.385	38	1.426	63	1.389	88	1.426
14	1.429	39	1.388	64	1.426	89	1.389
15	1.385	40	1.426	65	1.389	90	1.426
16	1.429	41	1.388	66	1.426	91	1.389
17	1.386	42	1.426	67	1.389	92	1.426
18	1.428	43	1.388	68	1.426	93	1.389
19	1.387	44	1.426	69	1.389	94	1.426
20	1.428	45	1.388	70	1.426	95	1.389
21	1.387	46	1.426	71	1.389	96	1.426
22	1.427	47	1.388	72	1.426	97	1.389
23	1.387	48	1.426	73	1.389	98	1.426
24	1.427	49	1.388	74	1.426	99	1.389
25	1.387	50	1.426	75	1.389	100	1.426

(VII-3) $$\gamma(\text{This Study}) = -\ 0.47605 \times 7.969 \times 10^{-19}$$

$$= -\ 3.794 \times 10^{-19}\ \text{Joules}\cdot\text{electron}^{-1}\ ,$$

which is 27% of the Grant and Batra value. The value of γ given in the APPENDIX IS

(A-49) $$\gamma(\text{Traditional}) = -2.779 \times 10^{-19}\ \text{Joules}\cdot\text{electron}^{-1}\ .$$

Thus, we must conclude that the 'no mixing' model of Grant and Batra is in error.

With the value of γ of (VII-3)

(VII-4) $$\Delta E(\text{band gap}) = -1.38 \times 10^{-1}\ (-3.794 \times 10^{-19})$$

$$= 5.236 \times 10^{-20}\ \text{Joules}\cdot\text{electron}^{-1}\ ,$$

which corresponds to a frequency of

(VI-5) $$\nu = \frac{5.236 \times 10^{-20}}{h}$$

$$= \frac{5.236 \times 10^{-20}}{6.626 \times 10^{-34}}$$

$$= 7.902 \times 10^{13}\ \text{Hertz}\ ,$$

which is in the near infrared.

At this point we must end this REPORT. When funds are available, EBL Theory will be applied to the study of the optical and thermodynamic properties of the poly (p-phenylene)'s.

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APPENDIX

MOLECULAR QUANTUM MECHANICS

A. GENERAL PRINCIPLES

Sir Isaac Newton, we are told, wrote to Robert Hooke, 'If I have seen further, it is by standing upon the shoulders of Giants.'[76] The modesty of the author of the Philosophiae Naturalis Principia Mathematica resulted in this self denigration of his momentous achievement. Only twice since Newton have the contributions of a single man been so great that he has been honored by the association of his name with an entire branch of physics. These two cases are J.C. Maxwell and the conjunction of electromagnetic theory and optics and A. Einstein and the theory of relativity. [The fact that both Newtonian mechanics and Maxwellian electromagnetics are derivable today from relativity theory in no way degrades the significance of the work of Newton and Maxwell.]

The fourth great system besides Newtonian mechanics, Maxwellian electromagnetics and Einsteinian mechanics is quantum mechanics. Unlike the other three systems, however, we cannot associate a single name with the system. No one great name stands out. This is the result, at least in part, of the fact that quantum mechanics is an unfinished system. Potentials, masses and changes are introduced in an *ad hoc* way. [In non-relativistic quantum mechanics spin also is introduced in an *ad hoc* way.] For energies of the order of magnitude of 10^{-13} Joules per particle present day quantum mechanics is less than satisfactory. For energies of the order of 10^{-19} Joules per particle, however, present day quantum mechanics in spite of all of its inadequacies works quite well. This, it should be noted, is the region of the energies of the chemistry of atoms and molecules.

In quantum mechanics the state of a system is represented by a vector (function). The measuring of the value of a physical parameter of the system is represented by a matrix (operator). If the result of multiplying the vector by the matrix (or the operating on the function with the operator) is the vector (or function) itself multiplied by a number, the number is called an <u>eigenvalue</u>, and the vector (function) is called an <u>eigenvector</u> (<u>eigenfunction</u>). The eigenvalue is the value of physical parameter which is obtained each time the measurement is made on the system when it is in the specified state (within experimental error).

If the result of the multiplication of the vector by the matrix is not the original vector multiplied by a number (scalar), then a different value will be obtained for the physical parameter each time the measurement is made. These concepts are represented mathematically by the following. Let $|\Psi_j\rangle$ be the vector representing the system in the j-th state, and let $(\tilde{M})$ be the matrix representing the measurement of a specific physical parameter. If $|\Psi_j\rangle$ is an eigenvector of $(\tilde{M})$, then

$$(\tilde{M})|\Psi_j\rangle = m_j|\Psi_j\rangle \quad , \tag{A-1}$$

where m_j is the eigenvalue.

We now multiply (A -1) on the left by the <u>dual</u> vector $\langle\Psi_j^*|$. Thus,

$$\langle\Psi_j^*|(\tilde{M})|\Psi_j\rangle = m_j\langle\Psi_j^*|\cdot|\Psi_j\rangle \quad ,$$

which is abbreviated

(A -2) $$\langle \Psi_j^* | \tilde{M} | \Psi_j \rangle = m_j \langle \Psi_j^* | \Psi_j \rangle$$

The eigenvalue appears outside of the vector multiplication because it is a scalar. The asterisk indicates complex conjugation. This is necessary since the components of the vectors can be complex numbers. (The functions can be complex functions.) Equation (A -2) can also be written

(A -3) $$m_j = \frac{\langle \Psi_j^* | \tilde{M} | \Psi_j \rangle}{\langle \Psi_j^* | \Psi_j \rangle} \ .$$

In the operator-function notation (A -3) becomes

(A -4) $$m_j = \frac{\int \Psi_j^* \, \tilde{M} \, \Psi_j \, d\Omega}{\int \Psi_j^* \, \Psi_j \, d\Omega} \ .$$

If $|\Psi_j\rangle$ is not an eigenvector of $(\tilde{M})$, then (A -1) no longer applies, but (A -3) and (A -4) still do. In these cases the m_j's are 'expectation values' (mean values) rather than eigenvalues. If the operator is 'integrate over the region r', then

(A -5) $$m_j = \frac{\int^{r} \Psi_j^* \, \Psi_j \, d\Omega}{\int^{\infty} \Psi_j^* \, \Psi_j \, d\Omega}$$

is the probability that the system when in the j-th state will be found in the region r.

The operators are generated by making the following replacements in the classical expression for the physical parameter:

(A -6) $$p_j \rightarrow -i\hbar \frac{\partial}{\partial x_j}$$ (j-th component of the linear momentum)

$$x_j \rightarrow x_j$$ (j-th component of the position vector)

$$E \rightarrow i\hbar \frac{\partial}{\partial t}$$ (energy of the system) ,

where $i = (-1)^{1/2}$ and $\hbar$ is Planck's constant divided by $2\pi (1.0546 \times 10^{-34}$ Joule sec). For a one particle system in the presence of a potential energy, V, the classical expression is

(A -7) $$\frac{p^2}{2m} + V = E \quad .$$

In the quantum mechanical formulation this becomes

(A -8) $$[\frac{1}{2m} (i\hbar)^2 \nabla^2 + V]\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

$$[\frac{-\hbar^2}{2m} \nabla^2 + V]\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad .$$

If the system consists of N particles, (A -8) becomes

(A -9) $$[\frac{-\hbar^2}{2} \sum_{j=1}^{N} \frac{1}{m_j} \nabla_j^2 + V]\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad ,$$

where ∇_j refers to the coordinates of the j-th particle. The potential energy, V, is a complicated combination of the coordinates of all of the particles. Because of this (A -9) cannot be solved directly for most systems. Various approximation techniques, however, have been developed.

To avoid the necessity of writing all of the (A -9) each time it is usually abreviated

(A -10) $$\tilde{H}\Psi = i\hbar \frac{\partial\Psi}{\partial t} ,$$

where

(A -11) $$\tilde{H} = -\frac{\hbar^2}{2} \sum_{j=1}^{N} \frac{1}{m_j} \nabla_j^2 + V$$

is the 'Hamiltonian operator'.

If the energy of the system is stationary with respect to time, the spacial and temporal functions of the state functions can be separated. Thus,

(A -12) $$\Psi(\vec{r},t) = \psi(\vec{r})\, e^{-i(E/\hbar)t} ,$$

where E is the energy of the system. The substitution of (A-12) into (A-10) yields

$$\tilde{H}\psi\, e^{-i(E/\hbar)t} = i\,\psi(\frac{-iE}{\hbar})\, e^{-i(E/\hbar)t}$$

or

(A -13) $$\tilde{H}\psi = E\psi .$$

It should be noted that the Hamiltonian operator does not contain time explicitly when the energy of the system is stationary. This is why the exponential can be factored out. In operator equations only terms to the left of the operators can be factored out.

Generally an equation like (A-13) has a large number of solutions (eigenvalues and eigenvectors) in which case it is written

$$\tilde{H}\psi_j = E_j \psi_j \tag{A-14}$$

[cf. (A-1)]. The 'j' here refers to the j-th eigenvector and not, as it did in (A-9) , to the j-th particle.

In any vector space a vector can be represented by a linear combination of a set of vectors called 'basis vectors'. Thus, in Euclidean 3-space any vector, $\vec{r}$, can be written as

$$\vec{r} = r_x\hat{e}_x + r_y\hat{e}_y + r_z\hat{e}_z \quad , \tag{A-15}$$

where the $\hat{e}$'s are 'unit vectors' as well as basis vectors. This principle also applies to Hilbert spaces which are infinite dimensional as they frequently are in quantum mechanics. Although basis vectors need not be orthogonal, it is convenient if they are.

An operator is said to be 'Hermetian' if

$$\langle\psi_k^*|\tilde{H}|\psi_j\rangle = \langle\psi_k^*|\tilde{H}^*|\psi_j\rangle \quad , \tag{A-16}$$

where $\tilde{H}^*$ is the complex conjugate of $\tilde{H}$. All the operators of quantum mechanics are Hermetian. Having all of the operators Hermetian ensures that all eigenvalues are real which they must be since they are the results of measurements. The real property of eigenvalues of Hermetian operators is shown by the following:

$$\tilde{H}|\psi_j\rangle = E_j|\psi_j\rangle \qquad \langle\psi_j^*|\tilde{H}^* = E_j^*\langle\psi_j^*|$$

$$\langle\psi_j^*|\tilde{H}|\psi_j\rangle = E_j\langle\psi_j^*|\psi_j\rangle \qquad \langle\psi_j^*|\tilde{H}|\psi_j\rangle = E_j^*\langle\psi_j^*|\psi_j\rangle$$

$$\langle\psi_j^*|\tilde{H}|\psi_j\rangle - \langle\psi_j^*|\tilde{H}^*|\psi_j\rangle = (E_j-E_j^*)\ \langle\psi_j^*|\psi_j\rangle \quad .$$

Since $\tilde{H}$ is Hermetian, the left side of the equation is zero. Since $\langle\psi_j^*|\psi_j\rangle$ is not zero, $E_j-E_j^*$ must be zero. This, however, can only be the case if E_j is real.

If the eigenvalues for two eigenvectors are <u>not</u> equal, then

$$\tilde{H}|\psi_j\rangle = E_j|\psi_j\rangle \qquad \langle\psi_k^*|\tilde{H}^* = E_k\langle\psi_k^*|$$

$$\langle\psi_k^*|\tilde{H}|\psi_j\rangle = E_j\langle\psi_k^*|\psi_j\rangle \qquad \langle\psi_k^*|\tilde{H}^*|\psi_j\rangle = E_k\langle\psi_k^*|\psi_j\rangle$$

$$\langle\psi_k^*|\tilde{H}|\psi_j\rangle - \langle\psi_k^*|\tilde{H}^*|\psi_j\rangle = (E_j-E_k)\ \langle\psi_k^*|\psi_j\rangle \quad .$$

By (A-16) the left hand side of the equation is zero. Since $E_j \neq E_k$, (A-17) $$\langle \psi_k^* | \psi_j \rangle = 0 \quad .$$

Thus, eigenvectors with different eigenvalues are automatically orthogonal.

It is somewhat difficult to work with a complete set of basis vectors when there are an infinite number of vectors in the set. The problem of working with infinite basis sets can usually be circumvented by the judicious choice of an approximate finite basis set. Assume that there is a Hamiltonian operator, $\tilde{H}'$, which is similar to, but not identical with, the $\tilde{H}$ of (A -14) and that

(A -18) $$\tilde{H}' Z = E Z$$

is not easily solved directly. We take Z as a linear combination of the ψ's. Thus,

(A -19) $$Z = \sum_{j=1}^{\infty} a_j \, \psi_j$$

$$\tilde{H}' \sum_{j=1}^{\infty} a_j \, \psi_j = E \sum_{j=1}^{\infty} a_j \, \psi_j \qquad \text{[by (A -18)]}$$

$$\left(\sum_{i=1}^{\infty} a_i^* \, \psi_i^* \right) \tilde{H}' \left(\sum_{j=1}^{\infty} a_j \, \psi_j \right) = \left(\sum_{i=1}^{\infty} a_i^* \psi_i^* \right) E \left(\sum_{j=1}^{\infty} a_j \, \psi_j \right)$$

and

(A -20) $$\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} a_i^* \, a_j \langle \psi_i^* | \tilde{H}' | \psi_j \rangle = E \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} a_i^* \, a_j \langle \psi_i^* | \psi_j \rangle$$

$$= E \sum_{j=1}^{\infty} a_j^* \, a_j \quad ,$$

where the last result is obtained on the assumption that the ψ's are both orthogonal and normalized (ortho-normal).

The a's are chosen so as to minimize E. The real ground state of the system will have the lowest possible value of E. Thus,

$$\sum_{j=1}^{\infty} a_j\langle\psi_i^*|\widetilde{H}'|\psi_j\rangle = \frac{\partial E}{\partial a_i^*}\sum_{j=1}^{\infty} a_j^* a_j + E\sum_{j=1}^{\infty} a_j \quad .$$

It should be noted that a_i is <u>linearly independent</u> of a_i^*. Thus, $\partial a_i/\partial a_i^* = 0$. Since the minimum value of E is desired, $\partial E/\partial a_i^*$ is set equal to zero, and

$$\text{(A -21)} \qquad \sum_{j=1}^{\infty} a_j(\langle\psi_i^*|\widetilde{H}'|\psi_j\rangle - E\delta_{ij}) = 0 \quad ,$$

where

$$\text{(A -22)} \qquad \begin{aligned} \delta_{ij} &= +1 \quad , & i &= j \\ &= 0 \quad , & i &\neq j \quad , \end{aligned}$$

and is known as the 'Kronecker delta'. The Kronecker delta is the matrix element of the 'identity' matrix. For (A -21) to have a non-trivial solution the determinant of the matrix must be equal to zero.

Since the ψ's are known, the integrals $\langle\psi_i^*|\widetilde{H}'|\psi_j\rangle$ can be evaluated -- at least by numerical integration. Generally only the negative valued integrals are retained. In this way the infinite a's problem is reduced to a finite a's problem. The variation technique just described can also be used for equations such as (A -10).

B. MOLECULAR APPROXIMATIONS

The simplest molecule, the hydrogen molecule ion, H_2^+, is a three body problem. The variables of (A -9) are not separable by any known techniques for more than two bodies. Thus, all of molecular quantum mechanics involves the use of approximation techniques. The first approxima-standardly envoked is the 'Born-Oppenheimer approximation' [7]. Since the nuclei are so much heavier than the electrons, the electrons will complete many oscillations in the time required for a nucleus to complete one oscillation. Thus, the nuclei are assumed to be stationary, and the properties of the electrons are studied relative to the 'stationary' nuclei. This analysis can be repeated for various nuclear positions. Standardly, however, only the equilibrium positions of the nuclei are considered.

The next approximation envoked is the separation of the 'inner' electron (which are not involved in bonding) for the 'outer' electrons (which are involved in bonding). The inner electrons are taken together with the nuclei as 'nuclear cores'. The outer electrons are separated by symmetry. Those electrons which are concentrated between the atoms which are bonded together and have cylindrical symmetry around the line connecting the nuclear centers are designated as 'σ-electrons' [sigma electrons]. The bonds between the hydrogens and the carbon of methane are σ-bonds.

In ethylene ($H_2C = CH_2$) the bonds between the hydrogens and the carbons are σ-bonds. One of the bonds between the carbon atoms is a σ-bond. The six atoms of ethylene in their equilibrium positions are co-planar. The second carbon-carbon bond is antisymmetric with respect to the plane of the atoms. The eigenvectors for these electrons are positive above the plane and negative below the plane. They are identically zero in the plane of the atoms. This type of bond is designated as a 'π-bond' [pi bond, pronounced 'pie' in English and 'pea' in Greek], and the electrons are designated as 'π-electrons'. The σ-bond of ethylene (two electrons) has a binding energy of 3.47×10^5 Joules per mole (83 kcal mole^{-1}). The π- bond (two electrons) has a binding energy of 2.64×10^5 Joules mole^{-1} (63 kcal mole^{-1}). The difference in binding energies is 8.3×10^4 Joules mole^{-1} (20 kcal mole^{-1}). This energy difference is sufficiently large to permit the treatment of the π-electrons separately from the σ-electrons. In this study only the π-electrons are analyzed.

C. LCAO-MO METHOD

In the LCAO-MO (linear combination of atomic orbitals - molecular orbital) method the eigenvector of (A -18) is a molecular orbital and the basis vectors of (A- 19) are atomic orbitals. For a complete basis vector set <u>all</u> of the atomic orbitals of <u>all</u> of the atoms should be used. This is, however, an infinite set. To avoid the problem of doing an infinite number of calculations we use an <u>incomplete</u> basis vector set. For the π-molecular orbitals only the $2p_y$- or $2p_z$- atomic orbitals are used. Furthermore, it should be noted, the basis vectors are not orthogonal. Equation (A -21) does not, therefore, apply. Except for a null vector any vector can be normalized to one. We shall, therefore, assume here that the atomic orbitals have been so normalized.

Let $|\psi_k\rangle$, $k = 1, \ldots, n$, be the eigenvectors (the molecular orbitals) of the Hamiltonian operator $\widetilde{H}$. Thus,

$$\widetilde{H}|\psi_k\rangle = E_k|\psi_k\rangle \tag{A -23}$$

or

$$\langle\psi_k|\widetilde{H}|\psi_k\rangle = E_k\langle\psi_k|\psi_k\rangle \quad . \tag{A -24}$$

It should be noted that we have multiplied (A -23) on the left by $\langle\psi_k|$ and not $\langle\psi_k^*|$. This is because we plan to use only real functions for the molecular orbitals.

Let $|u_i\rangle$, $i = 1, \ldots, n$, be the set of atomic orbitals. Since the basis vectors constitute an approximately complete set, other atomic orbitals making only minor contributions, we may write

$$|\psi_k\rangle = \sum_{i=1}^{n} \bar{z}_{ik}|u_i\rangle \quad . \tag{A -25}$$

The bar is placed over the coefficient z_{ik} to remind us that the $|\psi_k\rangle$'s are <u>not</u> normalized. When we carry out the normalizations, we will remove the bars.

The substitution of (A -25) into (A -24) yields

$$\sum_{j=1}^{n} \sum_{i=1}^{n} \bar{z}_{jk} \bar{z}_{ik}\langle u_j|\widetilde{H}|u_i\rangle = E_k \sum_{j=1}^{n} \sum_{i=1}^{n} \bar{z}_{jk} \bar{z}_{ik}\langle u_j|u_i\rangle \quad . \tag{A -26}$$

Equation (A-26) has two integrals which are elements of matrices. The first, the 'overlap' integral is

(A -27) $$\langle u_j | u_i \rangle = \int u_j \, u_i \, d\tau = \$_{ji} \quad .$$

Since the vectors are normalized,

(A -28) $$\$_{ji} = +1.00 \quad , \qquad \text{for} \quad j = i \quad .$$

Furthermore, let $\$$ be a 'standard' integral so that the off-diagonal elements may be written as

(A -29) $$\$_{ji} = \$\rho_{ji} \quad , \qquad j \neq i \quad .$$

By virtue of (A -28), and for later convenience, the diagonal elements of (ρ_{ji}) are taken to be zero. Thus,

(A -30) $$\rho_{ii} = 0.00 \quad .$$

[Note: The numbers of A -28) and A -30) are written as +1.00 and 0.00, respectively, rather than +1 and 0. This is because the theory is developed here for computer use, and computers distinguish between real numbers (+1.00 and 0.00) and integers (+1 and 0).] If (δ_{ji}) is the identity matrix, the matrix of the overlap integrals may be written as

(A -31) $$(\$_{ji}) = (\delta_{ji}) + \$(\rho_{ji}) \ .$$

By virtue of (A -27) $(\$_{ji})$, and hence (ρ_{ji}), is a symmetric matrix, i.e.,

(A -32) $$\$_{ji} = \$_{ij} \ .$$

The other integral of (A -26) is the 'exchange' integral,

(A-33) $$\langle u_j|\widetilde{H}|u_i\rangle = \int u_j \, \widetilde{H} \, u_i \, d\tau = \beta_{ji} \ .$$

Since $(\widetilde{H})$ is Hermetian, (β_{ji}) also is a symmetric matrix. The assumption is standardly made that

(A-34) $$\beta_{ji} = \beta\rho_{ji} \ , \qquad j \neq i \ ,$$

where β is a 'standard' integral.

Traditionally β_{ii} is represented q_{ii} and is called the 'Coulombic' integral, the 'standard' value of which is $\not{q}$. [The slash in $\not{q}$ is to distinguish between $\not{q}$, the standard value of the Coulombic integral, and q, the number of mers in the molecule.] A new 'standard' integral is now defined in terms of the three which have been defined already,

(A -35) $$\gamma = \beta - \not{q}\$ \ .$$

The general form for the diagonal terms of (β_{ji}) will be taken as

(A- 36) $$\beta_{ii} = \alpha_{ii} = \alpha + \delta_i \gamma \quad ,$$

where δ_i is an empirically determined parameter of the order of magnitude of one. The matrix of the exchange integrals now may be written as

(A -37) $$(\beta_{ji}) = (\{\alpha + \delta_i \gamma\} \, \delta_{ji}) + \beta(\rho_{ji})$$

$$= (\{\alpha + \delta_i[\beta - \alpha \$]\} \, \delta_{ji}) + \beta(\rho_{ji}) \qquad \text{[by (A -35)]}$$

$$= (\{\alpha[1 - \$\delta_i] + \beta\delta_i\} \, \delta_{ji}) + \beta(\rho_{ji})$$

$$= (\{\alpha\sigma_i + \beta\delta_i\} \, \delta_{ji}) + \beta(\rho_{ji}) \quad ,$$

where

(A -38) $$\sigma_i = 1 - \$\delta_i$$

or

(A -39) $$1 = \sigma_i + \$\delta_i$$

At this juncture the coefficients $\bar{z}_{ik}$ of (A -25) are not known. They are determined by requiring that the E_k's in (A -26) are <u>extrema</u> with respect to the $\bar{z}_{ik}$'s. This requires the taking of partial derivatives with respect to $\bar{z}_{ik}$ and setting $\partial E_k / \partial \bar{z}_{jk}$ equal to zero. This yields

(A -40) $$\sum_{i=1}^{n} \bar{z}_{ik}\,\beta_{ji} = E_k \sum_{i=1}^{n} \bar{z}_{ik}\,\$_{ji}\ ; \qquad j = 1, \ldots, n$$

[by (A -23) and (A -27)]

or

(A -41) $$(\beta_{ji})|\bar{z}_{ik}\rangle = E_k(\$_{ji})|\bar{z}_{ik}\rangle \ .$$

When (A -31) and (A -37) are used, (A- 41) becomes

(A -42) $$[(\{\text{¢}\sigma_i + \beta\delta_i\}\,\delta_{ji}) + \beta(\rho_{ji})]|\bar{z}_{ik}\rangle$$

$$= [E_k(\delta_{ji}) + \$E_k(\rho_{ji})]|\bar{z}_{ik}\rangle \ ,$$

(A -43) $$[(\{\text{¢}\sigma_i + \beta\delta_i - E_k\}\,\delta_{ji}) + (\{\beta - \$E_k\}\,\rho_{ji})]|\bar{z}_{ik}\rangle$$

$$= (0)|\bar{z}_{ik}\rangle \ ,$$

where (0) is the null matrix, or -- by virtue of (A -39) --

(A -44) $$[(\{\text{¢}\sigma_i + \beta\delta_i - E_k\left(\sigma_i + \$\delta_i\right)\}\,\delta_{ji})$$

$$+ (\{\beta - \$E_k\}\,\rho_{ji})]|\bar{z}_{ik}\rangle = (0)|\bar{z}_{ik}\rangle \ ,$$

(A -45) $$[(\{\sigma_i\left(\text{¢} - E_k\right) + \delta_i\left(\beta - \$E_k\right)\}\,\delta_{ji})$$

$$+ (\{\beta - \$E_k\}\,\rho_{ji})]|\bar{z}_{ik}\rangle = (0)|\bar{z}_{ij}\rangle \ ,$$

and, if $\beta - \$E_k \neq 0$,

$$(\text{A}-46) \qquad [(\{\sigma_i\lambda_k + \delta_i\}\,\delta_{ji}) + (\rho_{ji})]\,|\bar{z}_{ik}\rangle = (0)\,|\bar{z}_{ik}\rangle \quad ,$$

where

$$(\text{A}-47) \qquad \lambda_k = \frac{\not{q} - E_k}{\beta - \$E_k} \quad .$$

The solution of (A-46) will yield the <u>eigenvalues</u> λ_k and the <u>eigenvectors</u> $|\bar{z}_{ik}\rangle$; $k = 1, \ldots, n$.

From (A-47) we have

$$\beta\lambda_k - \$E_k\lambda_k = \not{q} - E_k \quad ,$$

$$E_k(1 - \$\lambda_k) = \not{q} - \beta\lambda_k \quad ,$$

or

$$(\text{A}-48) \qquad E_k = \frac{\not{q} - \beta\lambda_k}{1 - \$\lambda_k}$$

$$= \frac{\not{q} - (\gamma + \not{q}\$)\,\lambda_k}{1 - \$\lambda_k} \qquad \text{[by (A-35)]}$$

$$= \frac{\not{q}(1 - \$\lambda_k) - \gamma\lambda_k}{1 - \$\lambda_k}$$

$$= q - \frac{\gamma\lambda_k}{1 - \$\lambda_k}$$

It should be noted that

(A -49) $$\gamma = -2.779 \times 10^{-19} \text{ Joules molecule}^{-1}$$

$$= -6.022 \times 10^{23} \times 2.779 \times 10^{-19}$$

$$= -1.674 \times 10^{5} \text{ Joules mole}^{-1}$$

$$= -1.674 \times 10^{5}/4.184 \times 10^{3}$$

$$= -40.00 \text{ kcal mole}^{-1}$$

If (A -46) is to be solved by a computer technique, it is useful to rearrange it to

(A -50) $$[(\delta_i\delta_{ji}) + (\rho_{ji})]|\bar{z}_{ik}\rangle = (-\sigma_i\lambda_k\delta_{ji})|\bar{z}_{ik}\rangle$$

or

(A -51) $$[(-\delta_i\delta_{ji}) + (-\rho_{ji})]|\bar{z}_{ik}\rangle = (\sigma_i\lambda_k\delta_{ji})|\bar{z}_{ik}\rangle \quad .$$

If $\delta_i = 0.00$ for all i, $\sigma_i = +1.00$ for all i by (A -38). In this case (A -51) simplifies to

(A -52) $$(-\rho_{ji})|\bar{z}_{ik}\rangle = \lambda_k|\bar{z}_{ik}\rangle \quad .$$

If (ρ_{ji}) is tridiagonal, (A -52) can be solved by the 'EISPACK' (EIgensystem Subroutine Package) driver subroutine RST which yields the eigenvalues in ascending order as well as the eigenvectors. If (ρ_{ji}) is not tridiagonal, the driver subroutine RS can be used. In this routine a real symmetric matrix is reduced to a symmetric tridiagonal matrix for which the eigenvalues and eigenvectors are then obtained.

If $\delta_i \neq 0.00$ for all i, then the driver subroutine RSG must be used. The RSG subroutine determines the eigenvalues and eigenvectors for the real symmetric generalized eigenproblem A*X = (LAMBDA)*B*X. This is not as horrendous as it might appear to be at first since only the upper triangles of the A and B matrices are used.

The computer programs for the solution of (A-46) or (A-51) generally do not yield values of the $|\bar{z}_{ik}\rangle$'s such that

(A-53) $$\langle\psi_k|\psi_k\rangle = +1.00 \; ; \qquad k = 1, \ldots, n \; .$$

Thus, (A-25) should be rewritten as

(A-54) $$|\psi_k\rangle = N_k \sum_{i=1}^{n} \bar{z}_{ik}|u_i\rangle$$

or

(A-55) $$|\psi_k\rangle = \sum_{i=1}^{n} z_{ik}|u_i\rangle \quad ,$$

where

(A-56) $$z_{ik} = N_k \, \bar{z}_{ik}$$

The substitution of (A-54) into (A-53) yields

(A -57) $$+1.00 = \langle\psi_k|\psi_k\rangle = N_k^2 \sum_{j=1}^{n} \sum_{i=1}^{n} \bar{z}_{jk} \bar{z}_{ik} \langle u_j|u_i\rangle$$

$$= N_k^2 \sum_{j=1}^{n} \sum_{i=1}^{n} \bar{z}_{jk} \bar{z}_{ik} \$_{ji} \quad , \quad \text{[by (A -27)]}$$

or

(A -58) $$N_k = \{\langle\bar{z}_{kj}|\$_{ji}|\bar{z}_{ik}\rangle\}^{-1/2}$$

If $(\$_{ji})$ is tridiagonal,

(A -59, tridiagonal) $$N_k = \{\sum_{i=1}^{n} \bar{z}_{ik}^2 + 2 \sum_{i=1}^{n-1} \bar{z}_{ik} \bar{z}_{i+1,k} \$_{i,i+1}\}^{-1/2} \; ;$$

and, if $(\$_{ji})$ is pentadiagonal,

(A -59, pentadiagonal) $$N_k = \left\{\sum_{i=1}^{n} \bar{z}_{ik}^2 + 2 \sum_{i=1}^{n-1} \bar{z}_{ik} \bar{z}_{i+1,k} \$_{i,i+1} + 2 \sum_{i=1}^{n-2} \bar{z}_{ik} \bar{z}_{i+2,k} \$_{i,i+2}\right\}^{-1/2} .$$

If the electrons are assumed to be uncorrelated except for the Pauli exclusion principle [78], electron transitions can be treated as one electron transitions between individual molecular orbitals. Thus, the transition frequency for the transition from the r-th state to the t-th state, by virtue of (A -48), is given by

(A -60)

$$\begin{aligned}
\nu_{tr} &= h^{-1}(E_t - E_r) \\
&= h^{-1}\left(q - \frac{\gamma\lambda_t}{1 - \$\lambda_t} - q - \frac{-\gamma\lambda_r}{1 - \$\lambda_r}\right) \\
&= -\gamma h^{-1}\left(\frac{\lambda_t}{1 - \$\lambda_t} - \frac{\lambda_r}{1 - \$\lambda_r}\right) \\
&= 4.194 \times 10^{14}\left(\frac{\lambda_t}{1 - \$\lambda_t} - \frac{\lambda_r}{1 - \$\lambda_r}\right) \quad ,
\end{aligned}$$

where

(A -61)

$$h = 6.626 \times 10^{-34} \text{ Joule sec. ,}$$

and γ is given by (A -49).

D. GENERAL THEOREMS ON COORDINATE SYSTEMS

In the analysis which we shall begin in the next SECTION coordinate systems other than the Cartesian coordinate system will be used. It will, therefore, be useful to derive here the general theorems on coordinate systems and apply them to the spherical polar coordinate system and the elliptical coordinate system. We start with the concept of a vector in a 3-space as an ordered triple (x_1, x_2, x_3) such that

(A -62)

$$a(x_1, x_2, x_3) = (ax_1, ax_2, ax_3)$$

and

(A -63) $(x_1, x_2, x_3) + (y_1, y_2, y_3) = (x_1+y_1, x_2+y_2, x_3+y_3)$,

where a is a scalar (a number) and (y_1, y_2, y_3) is another vector. Furthermore, if we now use the Dirac notation for vectors,

(A -64) $\langle x_1, x_2, x_3 | y_1, y_2, y_3\rangle = x_1y_1 + x_2y_2 + x_3y_3$.

If $(x_1, x_2, x_3) = (y_1, y_2, y_3)$, then $x_1 = y_1$, $x_2 = y_2$, $x_3 = y_3$, and

(A -65)
$$\begin{aligned}\langle x_1, x_2, x_3 | x_1, x_2, x_3\rangle &= x_1^2 + x_2^2 + x_3^2 \\ &= x^2 ,\end{aligned}$$

where x is the magnitude of the vector (x_1, x_2, x_3).

The 'cosine' function may be defined by

(A -66) $\langle x|y\rangle = xy \cos(x,y)$

For simplicity in writing we shall use the following convention

(A -67)
$$\begin{aligned}|x_1, 0, 0\rangle &= |x_1\rangle \\ |0, x_2, 0\rangle &= |x_2\rangle \\ |0, 0, x_3\rangle &= |x_3\rangle\end{aligned}$$

These three vectors are orthognal, i.e.,

(A -68) $$\langle x_i | x_j \rangle = x_i^2 \, \delta_{ij} \quad ,$$

where $\delta_{ij} = 0.00$ if $i \neq j$, and $\delta_{ij} = +1.00$ if $i = j$ [the Kronecker delta, which is also -- as noted previously -- the elements of the unit matrix].

Another set of vectors can be defined in terms of the orthogonal set

(A -69) $$|y_\alpha\rangle = \sum_{i=1}^{3} a_{\alpha i} |x_i\rangle$$

$$= a_{\alpha i} |x_i\rangle \quad ,$$

where the Einstein summation convention is used in the last line. If the determinant of the matrix $(a_{\alpha i})$ is not zero, there exists another matrix such that

(A -70) $$|x_j\rangle = b_{j\beta} |y_\beta\rangle$$

Let the symbol $|\hat{x}_i\rangle$ represent a unit vector in the 'direction' of $|x_i\rangle$ and $|dx_i\rangle$ a vector in the 'direction' of $|x_i\rangle$ of magnitude dx_i. If

(A -71) $$|\hat{y}_\alpha\rangle = a_{\alpha i} |\hat{x}_i\rangle \quad ,$$

then

(A- 72) $$\langle x_j | y_\alpha \rangle = a_{\alpha i} \langle \hat{x}_j | \hat{x}_i \rangle$$

$$= a_{\alpha i}\, \delta_{ji}$$ [by (A-68) and the unit magnitude of the vectors]

$$= a_{\alpha j}$$

or

(A-73) $$\cos(\hat{x}_j, \hat{y}_\alpha) = a_{\alpha j}$$ [by (A-66) and the unit magnitude of the vectors] .

By the calculus we have

(A-74) $$dx_j = \frac{\partial x_j}{\partial y_\beta}\, dy_\beta \quad .$$

Since, by (A-70),

(A-75) $$|dx_j\rangle = b_{j\beta} |dy_\beta\rangle \ ,$$

$$\left|\frac{\partial x_j}{\partial y_\beta}\, dy_\beta\right\rangle = b_{j\beta} |dy_\beta\rangle \ ,$$ [by (A-74)]

and

$$\frac{\partial x_j}{\partial y_\beta} |dy_\beta\rangle = b_{j\beta} |dy_\beta\rangle \ ,$$

(A- 76) $$b_{j\beta} = \frac{\partial x_j}{\partial y_\beta} \ .$$

The differential displacement $|ds\rangle$ has the magnitude

(A-77) $$ds^2 = \langle dx_i | dx_i \rangle$$

$$= \langle \frac{\partial x_i}{\partial y_\alpha} dy_\alpha | \frac{\partial x_i}{\partial y_\beta} dy_\beta \rangle \qquad \text{[by (A-74)]}$$

$$= \frac{\partial x_i}{\partial y_\alpha} \frac{\partial x_i}{\partial y_\beta} dy_\alpha \, dy_\beta$$

$$= Y_{\alpha\beta} \, dy_\alpha \, dy_\beta \quad ,$$

where

(A-78) $$Y_{\alpha\beta} = \frac{\partial x_i}{\partial y_\alpha} \frac{\partial x_i}{\partial y_\beta} \quad .$$

The distance between two points on a coordinate line in the $|y_\alpha\rangle$ system along the vector $|y_\alpha\rangle$ is given by

(A-79) $$ds_\alpha = Y_{\alpha\alpha}^{1/2} \, dy_\alpha \quad .$$

The cosine of the vectors $\langle \hat{y}_\beta |$ and $| \hat{y}_\alpha \rangle$ is given by

(A-80) $$\cos(y_\beta, y_\alpha) = \langle \hat{y}_\beta | \hat{y}_\alpha \rangle$$

$$= a_{\beta j} \, a_{\alpha i} \langle \hat{x}_j | \hat{x}_i \rangle \qquad \text{[by (A-69)]}$$

$$= a_{\beta j} \, a_{\alpha i} \, \delta_{ji} \qquad \text{[by (A-68) and the unit magnitude of the vectors]}$$

$$= a_{\beta j} \, a_{\alpha j}$$

$$= \cos(y_\beta, x_j) \cos(y_\alpha, x_j) \qquad \text{[by (A-73)]} \quad .$$

By (A -64) $\langle \hat{y}_\beta | \hat{x}_j \rangle$ is a scalar. Thus, by the commutativity of the multiplication of real numbers

(A -81) $$\langle \hat{y}_\beta | \hat{x}_j \rangle = \langle \hat{x}_j | \hat{y}_\beta \rangle \quad ,$$

and

(A -82) $$\cos(y_\beta, x_j) = \cos(x_j, y_\beta)$$

Thus, by (A -80), we may write

(A -83) $$\cos(ds_\alpha, ds_\beta) = \cos(x_j, ds_\alpha) \cos(x_j, ds_\beta)$$

By the combination of (A -73) and (A -76), we may write

(A -84) $$\cos(ds_\alpha, ds_\beta) = \frac{\partial x_j}{\partial s_\alpha} \frac{\partial x_j}{\partial s_\beta}$$

By the calculus

(A -85) $$\frac{\partial x_j}{\partial s_\alpha} = \frac{\partial x_j}{\partial y_\gamma} \frac{\partial y_\gamma}{\partial s_\alpha} \quad ,$$

and by (A -79)

(A -86) $$\frac{\partial y_\gamma}{\partial s_\alpha} = Y_{\alpha\alpha}^{-1/2} \delta_{\gamma\alpha}$$

Thus,

$$(\text{A-87}) \qquad \begin{aligned} \cos(ds_\alpha, ds_\beta) &= \frac{\partial x_i}{\partial s_\alpha}\frac{\partial x_i}{\partial s_\beta} && [\text{by (A-84)}] \\ &= \frac{\partial x_i}{\partial y_\gamma}\frac{\partial y_\gamma}{\partial s_\alpha}\frac{\partial x_i}{\partial y_\delta}\frac{\partial y_\delta}{\partial s_\beta} && [\text{by (A-85)}] \\ &= \frac{\partial x_i}{\partial y_\gamma}\frac{\partial x_i}{\partial y_\delta} Y_{\gamma\gamma}^{-1/2}\,\delta_{\gamma\alpha}\,Y_{\delta\delta}^{-1/2}\,\delta_{\delta\beta} && [\text{by (A-86)}] \\ &= Y_{\gamma\delta}\,Y_{\gamma\gamma}^{-1/2}\,\delta_{\gamma\alpha}\,Y_{\delta\delta}^{-1/2}\,\delta_{\delta\beta} && [\text{by (A-78)}] \\ &= Y_{\alpha\beta}\,Y_{\alpha\alpha}^{-1/2}\,Y_{\beta\beta}^{-1/2} \; . \end{aligned}$$

If $|ds_\alpha\rangle$ and $|ds_\beta\rangle$ are orthogonal, the cosine is equal to zero, and

$$(\text{A-88}) \qquad Y_{\alpha\beta} = 0 \; .$$

Thus, for orthogonal coordinate systems only the $Y_{\alpha\alpha}$ terms in (A-77) appear. In such a coordinate system the volume element is given by

$$(\text{A-89}) \qquad \begin{aligned} d\tau &= \prod_\alpha ds_\alpha \\ &= \prod_\alpha Y_{\alpha\alpha}^{1/2}\,dy_\alpha && [\text{by (A-79)}] \; . \end{aligned}$$

In the spherical polar coordinate system the radius vector $|r\rangle$ makes an angle θ with the x_3 axis. Thus,

$$(\text{A-90}) \qquad 0 \le \theta \le \pi \; .$$

The projection of the $|r\rangle$ vector on the x_1, x_2-plane has the magnitude $r \sin \theta$. The $|r \sin \theta\rangle$ vector makes an angle ϕ with the x_1-axis. Thus,

(A -91) $$0 \leq \phi \leq 2\pi \quad ,$$

and furthermore

(A -92) $$\begin{aligned} x_1 &= r \sin \theta \cos \phi \\ x_2 &= r \sin \theta \sin \phi \\ x_3 &= r \cos \theta \ . \end{aligned}$$

By geometric arguments it can be shown that $|dr\rangle$, $|d\theta\rangle$ and $|d\phi\rangle$ are a mutually perpendicular triad. We shall, however, use (A -88) to prove it. By (III-92) and the calculus we have

(A -93) $$\begin{aligned} &\frac{\partial x_1}{\partial r} = \sin \theta \cos \phi && \frac{\partial x_1}{\partial \theta} = r \cos \theta \cos \phi && \frac{\partial x_1}{\partial \phi} = -r \sin \theta \sin \phi \\ &\frac{\partial x_2}{\partial r} = \sin \theta \sin \phi && \frac{\partial x_2}{\partial \theta} = r \cos \theta \sin \phi && \frac{\partial x_2}{\partial \phi} = -r \sin \theta \cos \phi \\ &\frac{\partial x_3}{\partial r} = \cos \theta && \frac{\partial x_3}{\partial \theta} = -r \sin \theta && \frac{\partial x_3}{\partial \phi} = 0 \quad , \end{aligned}$$

(A -94) $$\begin{aligned} Y_{r\theta} &= r \sin \theta \cos \theta \cos^2 \phi + r \sin \theta \cos \theta \sin^2 \phi - r \sin \theta \cos \theta \\ &= r \sin \theta \cos \theta - r \sin \theta \cos \theta \\ &= 0 \quad , \end{aligned}$$

(A -95) $$Y_{r\phi} = -r \sin^2 \theta \sin \phi \cos \phi + r \sin^2 \theta \sin \phi \cos \phi + 0$$

$$= 0 \quad ,$$

and

(A -96) $$Y_{\theta\phi} = -r^2 \sin \theta \cos \theta \sin \phi \cos \phi + r^2 \sin \theta \cos \theta \sin \phi \cos \phi + 0$$

$$= 0 \quad .$$

The expression for $d\tau$ is obtained from (A -89). Thus,

(A -97) $$Y_{rr} = \sin^2 \theta \cos^2 \phi + \sin^2 \theta \sin^2 \phi + \cos^2 \theta$$

$$= \sin^2 \theta + \cos^2 \theta$$

$$= 1 \quad ,$$

(A -98) $$Y_{\theta\theta} = r^2 \cos^2 \theta \cos^2 \phi + r^2 \cos^2 \theta \sin^2 \phi + r^2 \sin^2 \theta$$

$$= r^2 \cos^2 \theta + r^2 \sin^2 \theta$$

$$= r^2 \quad ,$$

(A -99) $$Y_{\phi\phi} = r^2 \sin^2 \theta \sin^2 \phi + r^2 \sin^2 \theta \cos^2 \phi + 0$$

$$= r^2 \sin^2 \theta \quad ,$$

and

(A -100) $$d\tau = (1)^{1/2}\,(dr)(r^2)^{1/2}\,(d\theta)(r^2 \sin^2 \theta)^{1/2}\,(d\phi)$$

$$= r^2 \sin \theta \; dr \; d\theta \; d\phi \quad .$$

The geometry of the elliptical coordinate system is developed in terms of the points $(-a, 0, 0)$ and $(+a, 0, 0)$. The distances from these points to an arbitrary point (x_1, x_2, x_3) are r_1 and r_2, respectively. The distance between the arbitrary point and the x_1-axis is h. Since $|h\rangle$ is perpendicular to $|\hat{x}_1\rangle$, it is parallel to the x_2, x_3-plane. Thus, the magnitude of its projection on the x_2, x_3-plane is also h. The angle between the projected h vector and $|\hat{x}_2\rangle$ is θ. Thus, we immediately have

(A-101) $$x_2 = h \cos \theta$$

and

(A -102) $$x_3 = h \sin \theta$$

The intersection of the h vector with the x_1-axis is at the point $(x_1, 0, 0)$. The distance from this point to $(-a, 0, 0)$ is $|a+x|$. The triangle formed by the points $(-a, 0, 0)$, (x_1, x_2, x_3) and $(x_1, 0, 0)$ is a right triangle with the right angle at $(x_1, 0, 0)$. Thus, by the Pythagorean relation

(A-103) $$r_1^2 = h^2 + (a+x_1)^2$$

$$= h^2 + a^2 + 2ax_1 + x_1^2$$

Similarly, for the triangle formed by the points $(+a, 0, 0)$, (x_1, x_2, x_3) and $(x_1, 0, 0)$,

$$r_2^2 = h^2 + (a-x_1)^2 \tag{A-104}$$

$$= h^2 + a^2 - 2ax_1 + x_1^2 \quad .$$

If we subtract (A-104) from (A-103), we obtain

$$r_1^2 - r_2^2 = 4ax_1$$

or

$$x_1 = \frac{r_1^2 - r_2^2}{4a} \tag{A-105}$$

$$= a\xi\eta \quad ,$$

where

$$\xi = \frac{r_1+r_2}{2a} \tag{A-106}$$

and

$$\eta = \frac{r_1-r_2}{2a} \quad . \tag{A-107}$$

If we add (A-104) and (A-103), we obtain

$$r_1^2 + r_2^2 = 2h^2 + 2a^2 + 2x_1^2 \quad ,$$

or

(A -108) $$h^2 = \frac{r_1^2+r_2^2}{2} - a^2 - x_1^2$$

$$= \frac{r_1^2+r_2^2}{2} - a^2 - \left(\frac{r_1^2-r_2^2}{4a}\right)^2 \qquad \text{[by (A -105)]}$$

$$= \frac{8a^2r_1^2 + 8a^2r_2^2 - 16a^4 - r_1^4 + 2r_1^2r_2^2 - r_2^4}{16a^2}$$

$$= \frac{(r_1^2 + 2r_1r_2 + r_2^2 - 4a^2)\ (4a^2 - r_1^2 + 2r_1r_2 - r_2^2)}{16a^2}$$

$$= \frac{[(r_1+r_2)^2 - 4a^2]\ [4a^2 - (r_1-r_2)^2]}{16a^2}$$

$$= \frac{16a^4}{16a^2}\left[\left(\frac{r_1+r_2}{2a}\right)^2 - 1\right]\left[1 - \left(\frac{r_1-r_2}{2a}\right)^2\right]$$

$$= a^2[\xi^2-1]\ [1-\eta^2] \qquad \text{[by (A -106) and (A -107)]} .$$

Thus, by (A -108), (A -101) and (A -102),

(A -109) $$x_2 = a(\xi^2-1)^{1/2}\ (1-\eta^2)^{1/2} \cos\theta$$

and

(A -110) $$x_3 = a(\xi^2-1)^{1/2}\ (1-\eta^2)^{1/2} \sin\theta \ .$$

In order to use (A -88) for the mutual orthogonality test, we must first derive the partial derivatives matrix. Thus,

(A -111)

$$\frac{\partial x_1}{\partial \xi} = a\eta \qquad \frac{\partial x_1}{\partial \eta} = a\xi \qquad \frac{\partial x_1}{\partial \theta} = 0$$

$$\frac{\partial x_2}{\partial \xi} = \frac{a\xi(1-\eta^2)^{1/2} \cos\theta}{(\xi^2-1)^{1/2}} \quad \frac{\partial x_2}{\partial \eta} = \frac{-a\eta(\xi^2-1)^{1/2} \cos\theta}{(1-\eta^2)^{1/2}} \quad \frac{\partial x_2}{\partial \theta} = -a(\xi^2-1)^{1/2}(1-\eta^2)^{1/2} \sin\theta$$

$$\frac{\partial x_3}{\partial \xi} = \frac{a\xi(1-\eta^2)^{1/2} \sin\theta}{(\xi^2-1)^{1/2}} \quad \frac{\partial x_3}{\partial \eta} = \frac{-a\eta(\xi^2-1)^{1/2} \sin\theta}{(1-\eta^2)^{1/2}} \quad \frac{\partial x_3}{\partial \theta} = a(\xi^2-1)^{1/2} (1-\eta^2)^{1/2} \cos\theta$$

from which we derive

(A -112)
$$\begin{aligned} Y_{\xi\eta} &= a^2\eta\xi - a^2\xi\eta \cos^2\theta - a^2\xi\eta \sin^2\theta \\ &= a^2\eta\xi - a^2\eta\xi \\ &= 0 \ , \end{aligned}$$

(A -113)
$$\begin{aligned} Y_{\xi\theta} &= -a^2\xi(1-\eta^2) \cos\theta \sin\theta + a^2\xi(1-\eta^2) \sin\theta \cos\theta \\ &= 0 \ , \end{aligned}$$

and

(A -114)
$$\begin{aligned} Y_{\eta\theta} &= a^2\eta(\xi^2-1) \cos\theta \sin\theta - a^2\eta(\xi^2-1) \sin\theta \cos\theta \\ &= 0 \ . \end{aligned}$$

Thus, we have a mutually orthogonal triad and can use (A -89) to calculate $d\tau$,

(A- 115) $$Y_{\xi\xi} = a^2\eta^2 + a^2\xi^2 \frac{(1-\eta^2)}{(\xi^2-1)} \quad ,$$

(A -116) $$Y_{\eta\eta} = a^2\xi^2 + a^2\eta^2 \frac{(\xi^2-1)}{(1-\eta^2)} \quad ,$$

(A -117) $$Y_{\theta\theta} = a^2(\xi^2-1)(1-\eta^2) \quad ,$$

and

(A -118) $$\begin{aligned} Y_{\xi\xi}\, Y_{\eta\eta}\, Y_{\theta\theta} &= \left[a^2\eta^2 + a^2\xi^2 \frac{(1-\eta^2)}{(\xi^2-1)}\right] \left[a^2\xi^2 + a^2\eta^2 \frac{(\xi^2-1)}{(1-\eta^2)}\right] \\ &\quad \cdot \left[a^2(\xi^2-1)(1-\eta^2)\right] \\ &= a^6[\eta^2(\xi^2-1) + \xi^2(1-\eta^2)]^2 \\ &= a^6[\eta^2\xi^2 - \eta^2 + \xi^2 - \xi^2\eta^2]^2 \\ &= a^6[\xi^2 - \eta^2]^2 \quad . \end{aligned}$$

Thus,

(A -119) $$d\tau = a^3[\xi^2 - \eta^2]\; d\xi\; d\eta\; d\theta \quad .$$

E. EVALUATION OF ATOMIC INTEGRALS

Since every atom beyond hydrogen constitutes a multi-body problem, (A -9) cannot be solved for atoms as well as for molecules (except for the hydrogen atom, of course). It is, therefore, necessary to introduce approximations for the atomic orbitals. For this purpose we have used what are known as 'Slater orbitals' [63, 64, 65]. The rules for setting up Slater orbitals are fairly complicated since they are used for any orbital for any atom. Since we shall be interested in just 2p-orbitals, we shall consider only the rules for these orbitals.

The Slater orbitals are hydrogen-like orbitals which have been modified to take into account the partial shielding of the nucleus by the other electrons in the atom. In units of a full electron charge of 1.00, for 2p-electrons the shielding factor is 0.85 for each 1s electron and 0.35 for each of the other 2-shell electrons. With the 'effective nuclear charge', w, the 2p-orbitals are given by

$$u(2p_j) = N_{2p}\, x_j\, e^{-wr/2} , \tag{A -120}$$

where N_{2p} is the normalization factor, x_j is the j-th Cartesian coordinate, r is spherical polar radial coordinate and is in units of the Bohr radius (5.29×10^{-11} meters).

For carbon the nuclear charge in electron units is 6. There are two 1s-electrons and three other 2-shell electrons. Thus,

$$\begin{aligned} w(\text{carbon}) &= 6 - 2 \times 0.85 - 3 \times 0.35 \\ &= 3.25 . \end{aligned} \tag{A -121}$$

Similarly,

(A -122) $$w(\text{nitrogen}) = 7 - 2 \times 0.85 - 4 \times 0.35$$
$$= 3.90 \ ,$$

and

(A -123) $$w(\text{oxygen}) = 8 - 2 \times 0.85 - 5 \times 0.35$$
$$= 4.55 \ .$$

The form of (A -120) indicates that the same normalization factor is used for all three 2p-functions. We shall now demonstrate that this is indeed the case. For $j = 1$

(A -124) $$\int u^* u\,d\tau = N_1^2 \int x_1^2\, e^{-wr}\, d\tau \qquad \text{[by (A -129)]}$$

$$= N_1^2 \int r^2 \sin^2\theta \cos^2\phi\, e^{-wr}\, d\tau \qquad \text{[by (A -92)]}$$

$$= N_1^2 \iiint r^2 \sin^2\theta \cos^2\phi\, e^{-wr}\, r^2 \sin\theta\, dr\, d\theta\, d\phi$$
$$\text{[by (A- 100)]}$$

$$= N_1^2 \iiint r^4 \sin^3\theta \cos^2\phi\, e^{-wr}\, dr\, d\theta\, d\phi$$

$$= N_1^2 \int_0^{2\pi} \cos^2\theta\, d\theta \int_0^{\pi} \sin^3\theta\, d\theta \int_0^{\infty} r^4 e^{-wr}\, dr$$

$$= N_1^2 \left[\frac{\theta}{2} + \frac{\sin 2\phi}{4}\right]_0^{2\pi} \cdot \left[-\cos\theta + \frac{\cos^3\theta}{3}\right]_0^{\pi}$$

$$\cdot \left[\frac{-e^{-wr}}{w^5}\{(wr)^4 + 4(wr)^3 + 12(wr)^2 + 24wr + 24\}\right]_0^{\infty}$$

$$= N_1^2[\pi] \cdot [1 - \tfrac{1}{3} + 1 - \tfrac{1}{3}]\ [w^{-5}(24)]$$

$$= N_1^2[\tfrac{4\pi}{3}]\ [24w^{-5}]$$

$$= N_1^2[32\pi\ w^{-5}] \ .$$

When the integral is set equal to one,

(A -125) $$N_1 = [w^5/32\pi]^{1/2}$$

For $j = 2$,

(A -126) $$\int u^* u d\tau = N_2^2 \int x_2^2 \, w^{-wr} \, d\tau$$ [by (A -120)]

$$= N_2^2 \int r^2 \sin^2 \theta \sin^2 \phi \, e^{-wr} \, d\tau$$ [by (A -92)]

$$= N_2^2 \int\int\int r^2 \sin^2 \theta \sin^2 \phi \, e^{-wr} \, r^2 \sin \theta \, dr \, d\theta \, d\phi$$

[by (A -100)]

$$= N_2^2 \int\int\int r^4 \sin^3 \theta \sin^2 \phi \, e^{-wr} \, dr \, d\theta \, d\phi$$

$$= N_2^2 \int_0^{2\pi} \sin^2 \phi \, d\phi \int_0^{\pi} \sin^3 \theta \, d\theta \int_0^{\infty} r^4 e^{-wr} \, dr$$

$$= N_2^2 \left[\frac{\phi}{2} - \frac{\sin 2\phi}{4}\right]_0^{2\pi} \cdot [\tfrac{4}{3}] \, [24 \, w^{-5}]$$

$$= N_2^2 [32\pi \, w^{-5}] \; .$$

For $j = 3$,

$$(A-127) \qquad \int u^* u\, d\tau = N_3^2 \int x_3^2\, e^{-wr}\, d\tau \qquad \text{[by (A-120)]}$$

$$= N_3^2 \int r^2 \cos^2 \theta\, e^{-wr}\, d\tau \qquad \text{[by (A-92)]}$$

$$= N_3^2 \iiint r^2 \cos^2 \theta\, e^{-wr}\, r^2 \sin \theta\, dr\, d\theta\, d\phi \qquad \text{[by (A-100)]}$$

$$= N_3^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta \cos^2 \theta\, d\theta \int_0^{\infty} r^4\, e^{-wr}\, dr$$

$$= N_3^2 [2\pi] \cdot \left[\frac{-\cos^3 \theta}{3}\right]_0^{\pi} \cdot [24\, w^{-5}]$$

$$= N_3^2 [2\pi] \cdot [\tfrac{1}{3} + \tfrac{1}{3}] \cdot [24\, w^{-5}]$$

$$= N_3^2 [32\pi\, w^{-5}] \quad .$$

For the evaluation of overlap integrals we must consider the case in which the values of w are the same for the two atomic orbitals and the case in which the values of w are different. Let w_1 be the value of w for the orbital at $(-a, 0, 0)$ and w_2 be the value of w for the orbital at $(+a, 0, 0)$. For the sake of specificity we shall assume

$$(A-128) \qquad w_2 = w_1 + 2\Delta \quad ,$$

where

(A -129) $$\Delta \geq 0 .$$

The factor of two in (A -128) is for convenience as will be seen shortly.

We shall assume that the atomic orbitals are $2p_2$-orbitals. By (A -120),

(A -130) $$\langle u_2|u_1\rangle = \int N_2 x_2\, e^{-w_2 r_2/2}\, N_1 x_2\, e^{-w_1 r_1/2}\, d\tau$$

$$= N_1 N_2 \int x_2^2\, e^{-w_1 r_1/2}\, e^{-(w_1+2\Delta) r_2/2}\, d\tau \qquad \text{[by (A -128)]}$$

$$= N_1 N_2 \int a^2(\xi^2-1)(1-\eta^2) \cos^2\theta\, e^{-w_1(r_1+r_2)/2}\, e^{-r_2\Delta}\, d\tau$$

[by (A -109)]

$$= N_1 N_2 \iiint a^2(\xi^2-1)(1-\eta^2) \cos^2\theta$$

$$\cdot\, e^{-w_1(r_1+r_2)/2}\, e^{-r_2\Delta}\, a^3(\xi^2-\eta^2)\, d\xi\, d\eta\, d\theta$$

[by (A -119)]

$$= N_1 N_2\, a^5 \iiint (\xi^2-1)(1-\eta^2)(\xi^2-\eta^2) \cos^2\theta$$

$$\cdot\, e^{-w_1(r_1+r_2)/2}\, e^{-r_2\Delta}\, d\xi\, d\eta\, d\theta \quad .$$

By (A -106) and (A -107)

(A -131) $$r_1+r_2 = 2a\xi$$

and

$$\xi-\eta = \frac{r_2}{a}$$

or

(A -132) $$r_2 = a(\xi-\eta) \quad .$$

Furthermore,

(A -133) $$(1-\eta^2)(\xi^2-\eta^2) = \xi^2 - (\xi^2+1)\eta^2 + \eta^4 \quad .$$

Thus, (A -130) becomes

(A -134) $$\langle u_2|u_1\rangle = N_1N_2\, a^5 \int_0^{2\pi} \cos^2\theta \int_{+1}^{\infty} e^{-w_1 a\xi}\, e^{-a\xi\Delta}(\xi^2-1)$$

$$\cdot \int_{-1}^{+1} [\xi^2 - (\xi^2+1)\eta^2 + \eta^4]\, e^{a\eta\Delta}\, d\eta\, d\xi$$

$$= N_1N_2\, a^5\pi \int_{+1}^{\infty} e^{-(w_1+\Delta)a\xi}(\xi^2-1) \int_{-1}^{+1}$$

$$\cdot\, e^{a\eta\Delta}[\xi^2 - (\xi^2+1)\eta^2 + \eta^4]\, d\eta\, d\xi \quad .$$

We shall consider three cases of (A -134) -- both u_1 and u_2 are carbon orbitals, u_1 is a carbon orbital and u_2 is a nitrogen orbital, and u_1 is a carbon orbital and u_2 is an oxygen orbital.

F. THE CARBON-CARBON OVERLAP INTEGERS

For the carbon-carbon case $\Delta = 0$ in (A -134)

$$(\text{A -135}) \quad \langle u_2|u_1\rangle = N_C^2\, a^5 \pi \int_{+1}^{\infty} e^{-w_C a\xi} (\xi^2-1) \int_{-1}^{+1} [\xi^2-(\xi^2+1)\eta^2+\eta^4]\, d\eta\, d\xi$$

$$= N_C^2\, a^5 \pi \int_{+1}^{\infty} e^{-w_C a\xi} (\xi^2-1)\left[\xi^2\eta - \frac{(\xi^2+1)\eta^3}{3} + \frac{\eta^5}{5}\right]_{-1}^{+1} d\xi$$

$$= N_C^2\, a^5 \pi \int_{+1}^{\infty} e^{-w_C a\xi} (\xi^2-1)\left[2\xi^2 - \frac{2(\xi^2+1)}{3} + \frac{2}{5}\right] d\xi$$

$$= \frac{2N_C^2\, a^5 \pi}{15} \int_{+1}^{\infty} e^{-w_C a\xi} (\xi^2-1)[15\xi^2-5\xi^2-5+3]\, d\xi$$

$$= \frac{2N_C^2\, a^5 \pi}{15} \int_{+1}^{\infty} e^{-w_C a\xi} (\xi^2-1)(10\xi^2-2)\, d\xi$$

$$= \frac{4N_C^2\, a^5 \pi}{15} \int_{+1}^{\infty} e^{-w_C a\xi} (\xi^2-1)(5\xi^2-1)\, d\xi$$

$$= \frac{4N_C^2\, a^5 \pi}{15} \int_{+1}^{\infty} e^{-w_C a\xi} (5\xi^4-6\xi^2+1)\, d\xi \ ,$$

where the subscript '1' has been replaced by the subscript 'C' for carbon. At this point it is necessary to invoke the standard indefinite integral

$$(\text{A-136}) \quad \int x^n\, e^{ax}\, dx = \frac{e^{ax}}{a^{n+1}} [(ax)^n - n(ax)^{n-1} + n(n-1)(ax)^{n-2} - \cdots + (-1)^n\, n!] \ ,$$

where n is a non-negative integer. The three integrals of interest are

$$(\text{A -137})\qquad \int_{+1}^{\infty} e^{-w_C a\xi}\, d\xi = \frac{-1}{w_C a}\, e^{-w_C a\xi}\Big|_{+1}^{\infty}$$

$$= (w_C a)^{-1}\, e^{-w_C a} \quad ,$$

$$(\text{A -138})\qquad \int_{+1}^{\infty} \xi^2\, e^{-w_C a\xi}\, d\xi = \left[\frac{e^{-w_C a\xi}}{(-w_C a)^3}\, \{(-w_C a\xi)^2 - 2(-w_C a\xi) + 2\}\right]_{+1}^{\infty}$$

$$= \frac{e^{-w_C a}}{(w_C a)^3}\, \{(w_C a)^2 + 2(w_C a) + 2\}$$

$$= e^{-w_C a}\{(w_C a)^{-1} + 2(w_C a)^{-2} + 2(w_C a)^{-3}\} ,$$

and

$$(\text{A -139})\qquad \int_{+1}^{\infty} \xi^4\, e^{-w_C a\xi}\, d\xi = \left[\frac{e^{-w_C a\xi}}{(-w_C a)^5}\, \{(-w_C a\xi)^4 - 4(-w_C a\xi)^3 + 12(w_C a\xi)^2 \right.$$

$$\left. - 24(-w_C a\xi) + 24\}\right]_{+1}^{\infty}$$

$$= \frac{e^{-w_C a}}{(w_C a)^5}\, \{(w_C a)^4 + 4(w_C a)^3 + 12(w_C a) + 24(w_C a) + 24\}$$

$$= e^{-w_C a}\{(w_C a)^{-1} + 4(w_C a)^{-2} + 12(w_C a)^{-3}$$

$$+ 24(w_C a)^{-4} + 24(w_C a)^{-5}\} .$$

We now evaluate (A -135) as

(A -140) $$\langle u_2|u_1\rangle = \frac{4N_C^2 a^5 \pi}{15}\Big[5\, e^{-w_C a}\{(w_C a)^{-1} + 4(w_C a)^{-2} + 12(w_C a)^{-3} + 24(w_C a)^{-4} + 24(w_C a)^{-5}\} - 6e^{-w_C a}\{(w_C a)^{-1} + 2(w_C a)^{-2} + 2(w_C a)^{-3}\} + e^{-w_C a}(w_C a)^{-1}\Big]$$

$$= \frac{4N_C^2 a^5 \pi}{15}\Big[e^{-w_C a}\Big]\Big[8(w_C a)^{-2} + 48(w_C a)^{-3} + 120(w_C a)^{-4} + 120(w_C a)^{-5}\Big]$$

$$= \frac{32N_C^2 a^5 \pi}{15}\Big[e^{-w_C a}\Big]\Big[(w_C a)^{-2} + 6(w_C a)^{-3} + 15(w_C a)^{-4} + 15(w_C a)^{-5}\Big] .$$

Since

(A -121) $$w_C = 3.25 ,$$

and

(A -125) $$N_C = [w_C^5/32\pi]^{1/2} ,$$

(A -141) $$\frac{32N_C^2\pi}{15} = \frac{32\pi}{15}\cdot\frac{w_C^5}{32} = \frac{w_C^5}{15} = 24.173 .$$

We shall be interested in carbon-carbon distances from 1.19×10^{-10} meters to 1.47×10^{-10} meters. The parameter a is half this distance measured in Bohr radii (5.29×10^{-11} meters). Thus, the range of interest of a is 1.12 to 1.39. The values of \$ for these values of a are listed in TABLE A -1. The carbon-carbon distance in benzene is 1.39×10^{-10} meters. In Bohr radii this is 2.628. Thus, a for benzene is 1.314. The value of \$ in TABLE A -1 for a = 1.315 is 0.248. This is the reason that the 'traditional' value for the carbon-carbon overlap integral is taken as 1/4.

TABLE A-1

CARBON-CARBON

OVERLAP INTEGRALS

a (in Bohr radii)	$	a (in Bohr radii)	$
1.120	0.345	1.265	0.271
1.125	0.343	1.270	0.268
1.130	0.339	1.275	0.266
1.135	0.337	1.280	0.264
1.140	0.334	1.285	0.261
1.145	0.332	1.290	0.259
1.150	0.328	1.295	0.257
1.155	0.326	1.300	0.254
1.160	0.323	1.305	0.252
1.165	0.321	1.310	0.250
1.170	0.318	1.315	0.248
1.175	0.315	1.320	0.246
1.180	0.313	1.325	0.244
1.185	0.310	1.330	0.241
1.190	0.307	1.335	0.239
1.195	0.305	1.340	0.237
1.200	0.302	1.345	0.235
1.205	0.300	1.350	0.233
1.210	0.297	1.355	0.231
1.215	0.295	1.360	0.228
1.220	0.292	1.365	0.227
1.225	0.290	1.370	0.224
1.230	0.287	1.375	0.222
1.235	0.285	1.380	0.220
1.240	0.282	1.385	0.219
1.245	0.280	1.390	0.216
1.250	0.277	1.395	0.214
1.255	0.275	1.400	0.213
1.260	0.273		

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