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ANALYSIS AND APPLICATION OF THE  
ITERATIVE METHOD AND RELATED STABILITY PROBLEMS  
IN M.O. CALCULATIONS

by

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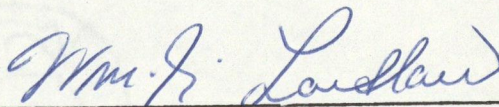
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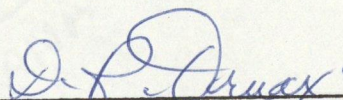
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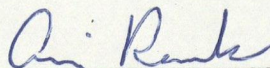
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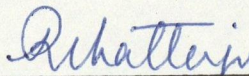
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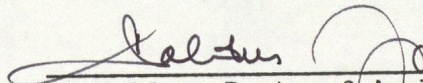
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## ABSTRACT

A self-consistent perturbation theory is used to obtain closed-form expressions for the density matrix elements to first order for the iterative procedure. The validity of the approximations involved to get the closed-form expressions is tested against a few  $\pi$ -electron systems. A similar analysis, but different in mathematical approach, is carried out for infinite networks. With the iterative method in its full form, bond length calculations were done for alternant and non-alternant hydrocarbons and the results are reported. The symmetry 'dilemma' that results from these calculations is discussed in connection with the 'singlet' stability of the Hartree-Fock solutions.

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TO

MY PARENTS

“ ஊழையும் உப்பக்கம் காண்பர் ; உலகின்தித்  
நாழாது உஞ்ஞ பவர் ”

திருவள்ளுவர்

"THOSE WHO WORK HARD AND THOSE WHO DESERVE SHALL EVENTUALLY FIND IT".

TIRUVALLUVAR  
(a Tamil Saint)

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## GLOSSARY OF SYMBOLS

$f$	The sigma energy function
$i,j,k,\ell,m,n$	The molecular orbital indices
$p,q,r,s,t,u,v,w$	The indices to denote the centers
$\alpha$	The coulomb integral
$\beta$	The bond integral
$\gamma_{rr}$	The one center repulsion integral
$\gamma_{rs}$	The two center repulsion integral
$\delta$	The perturbation parameter in the bond order dependent method
$\pi$	The polarizability matrix
$\omega$	The perturbation parameter in the charge-dependent method
$\underline{\Omega}$	The 'residual' polarizability matrix
$\lambda$	The lowest eigenvalue of the stability matrix
$\eta$	The occupancy number
$d_{U_j}$	The mixing coefficient
$ \chi_r\rangle,  \chi_s\rangle$	Atomic orbital basis
$k$	The alternation parameter
$\xi$	An empirical parameter in Salem's relation
$N$	Total number of pi-electrons
$H_{rr}$	The diagonal Hückel element
$F_{rr}$	The diagonal Fock element
$P_{rr}$	The charge density
$P_{rs}$	The bond order

$H_{rr}^{\text{core}}, \bar{H}_{rr}, \bar{H}_{rs}$	The core integral in the SCF method
$\hat{H}_{\text{eff}}$	Effective one electron hamiltonian
$H_{rs}$	The off-diagonal Hückel element
$E_i$	Energy of the molecular orbital
$C_{si}$	The orbital coefficient
$\Delta E_i^j$	Excitation energy
P,Q,R,S,T,U,V	The 'pair-notation' for the centers
I,J,K,L,M,N	The pair-notation for the molecular orbitals
$\pi$	3.14 - radians
E	The electronic energy
$ \phi\rangle$	Atomic orbital basis set
$ \psi\rangle$	Perturbed molecular orbitals
$\underline{A}$	Row vector of paired coefficients
$\underline{E}$	Diagonal energy matrix in the 'pair-notation'
H	The perturbation in a column vector
$\Delta P$	The difference between the density matrix elements
$R_{rs}$	The bond distance between centers r and s
$R_Q$	The bond distance between two centers in the 'paired-notation'
T	The total energy, the sum of sigma and pi energy
$E_\sigma$	Sigma electronic energy
$E_\pi$	pi-electronic energy
$A_{U_1 U_2}$	The diagonal matrix elements of the 'stability' matrix
$B_{U_1 U_2}$	The off-diagonal elements of the 'stability' matrix



$P$	The density matrix in the column vector
$\Delta P$	The difference in the column vectors of the density matrix elements
$ \Phi\rangle$	An arbitrary Slater determinant
$ \Phi_0\rangle$	The ground state configuration
$\Psi_1$	Molecular spin orbital
$A$	The matrix in the super 'stability' matrix
$D$	The column vector of mixing coefficients
$P$	The super column vector of the density matrix elements
$E$	The elliptic integrals of the second kind
$K$	The elliptic integrals of the first kind
$\Lambda$	The 'coupling' constant
$P_{\text{std}}$	Standard bond order
$R_{\text{std}}$	Standard bond length

## CHAPTER 1

### INTRODUCTION

#### 1.10: PURPOSE

This thesis is concerned with a study of a method of obtaining approximate values for the bond orders (and hence bond lengths) for conjugated  $\pi$ -electron systems of interest to chemists. As in nearly all realistic chemical problems, the methods of calculation are, by necessity, approximate. There are a number of mathematical methods available with which the problem can be attacked. Essentially all such methods involve an approximate representation of the physics of the problem from which is extracted a solution. This solution may then be used to calculate the relevant property directly or it may be improved by successive approximations. In the present case the method chosen (for reasons outlined in Chapter 2) is the so-called iterative scheme that takes a simple and readily accessible description and by a suitably chosen perturbation, properly parametrized, successively "improves" the result. Such a process raises a number of questions. For example, How does one choose the perturbation? What sort of parametrization is required? Does the procedure indeed converge to a unique solution? How rapidly does it converge? Can one analyse the procedure to obtain some insight into the final self-consistent form? All of these questions are non-trivial but not

all are normally considered. For example, the convergence of the self-consistent scheme in M.O. calculations is normally taken for granted but as pointed out by Schwartz<sup>1</sup> the convergence is not fully understood. Another example is that until recently little attention has been directed to the stability of molecular orbital descriptions obtained by solution of Hartree-Fock equations. Even such a fundamental concept as the conservation of symmetry in such calculations has been tacitly assumed but again this is not always so. These questions with specific reference to iterative methods prompted the investigations leading to much of the material reported in this thesis. In addition to carrying out such investigations, we have also applied the method to the calculation of a specific property of a number of conjugated pi-electron systems.

#### 1.20: RESUME

The iterative method described in Chapter 2 turns on two equations, one relating the bond order to the bond length and the other allowing one to set up the hamiltonian matrix elements for the new iteration from the bond order elements obtained in the previous iteration. Further, to adapt the method to several classes of pi-electron systems, a flexible parameter,  $\delta$ , which can be selected for a given class has been introduced into the second equation on which the iterative cycle rests. The success and the adaptability of this method requires that the procedure converges for appropriate  $\delta$  values and that it yields results in agreement

with the experimental data. To this end, we examined the convergence of the iterative method in some detail.

The investigation of the convergence of the iterative method has been carried out theoretically and numerically. The theoretical analysis follows the general perturbation theory. Based on this, general expressions were obtained for the density matrices at all stages of the iterative cycle under the L.C.A.O.-M.O. approximation. The equations that led to the convergence criterion were then derived. The description of the analysis is delineated in Chapter 3. To illustrate the usefulness of the approach, continuant matrices which are a representation of linear polyenes were considered in Chapter 4.

As a special case in our analysis we also considered infinite periodic networks. The convergence criterion and the breakdown point in the iterative method were treated in Chapter 5. To add support to the theoretical analysis, numerical investigations were also carried out for the infinite network.

In Chapter 6 we discuss the appropriate choice of values for  $\delta$  for two classes of alternant hydrocarbons and also for a class of non-alternant hydrocarbons and present the results of the applications of the iterative method with these values.

In the process of our calculations, it appeared that for certain systems, for example pentalene and heptalene, an initial symmetry ( $D_{2h}$ ) is lost and the process converges to a new symmetry ( $C_{2h}$ ). Some discussion of this is provided in Chapter 7,

in particular, the singlet instability associated with the symmetry problem of the Hartree-Fock solution. This investigation bears some resemblance to that of Paldus and Cizek<sup>2</sup> who observed that where the instability has occurred, the alternative stable solution is found to belong to a lower symmetry. A description of the examination of the stability of the Hartree-Fock solution for pentalene and heptalene and a discussion of our results is provided.

## CHAPTER 2

### ITERATIVE TECHNIQUES

#### 2.10: INTRODUCTION

Within the context of approximate schemes, methods of very general applicability have been developed and have found ready use. For example SCF-MO-PPP<sup>†</sup> schemes have been used for calculating many properties. However, schemes with the flexibility necessary to provide a wide variety of properties with reasonable accuracy are complex and frequently require heavy use of computing time. As a result, simpler schemes specifically designed for the calculations of a particular property have been developed. Such methods generally involve two parts: an appropriately parametrized relation between the observable quantity and a quantity calculated from the approximate mathematical description of the molecule. The latter quantity may, in itself, be the result of an iterative calculation wherein the quantities obtained from a given representation of the hamiltonian are used to define an improved hamiltonian with which a new value may be calculated. Although numerical calculations generally indicate that under certain restrictions the iterative method converges, there is a need to determine analytically the conditions under which the iterative method converges, to examine the convergent form and for infinite systems analyse the functional characteristics of the approach to self-consistency. To this end, we make reference to the principle iterative methods and use the perturbation theoretic approach to examine an iterative scheme for

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<sup>†</sup> Self-consistent field molecular orbital Pariser-Parr-Pople.

calculating bond orders.

## 2.20: THE NATURE OF ITERATIVE METHODS

There are many iterative methods<sup>3</sup> quite widely used in numerical analysis to obtain a better solution from an approximate solution or to solve an inhomogeneous problem. For example, integral equations<sup>4</sup> are customarily solved by an iterative method; an elementary iteration-variation procedure for solving the Schrödinger equation by the partitioning technique suggested by Löwdin is another instance.<sup>5</sup> The iterative methods are, in general, characterized either by successive approximations or successive substitutions. For example, to solve linear integral equations, the successive approximation method or the successive substitution method has been used. In both cases, the conditions under which the method would converge have been well demonstrated.<sup>4</sup>

The iterative methods that we will discuss use the idea of the successive substitution. Depending upon the property we wish to calculate, the nature of the method and the functional relations involved change. In the following, we will consider two such methods which have been used in MO calculations - one is the charge-dependent<sup>6-14</sup> and the other the bond-order dependent method.<sup>15-20</sup>

### 2.201: The Charge-Dependent Method

In the self-consistent field theory (SCF), the diagonal Fock matrix element,  $F_{rr}$ , of the effective hamiltonian at atom  $r$  depends on the charge-density,  $P_{rr}$ , at  $r$  and on the charge-densities at all other centers and it is given by:

$$F_{rr} = H_{rr}^{\text{core}} + \frac{1}{2} P_{rr} \gamma_{rr} + \sum_{s \neq r} P_{ss} \gamma_{rs} \quad (2-1)$$



where

$$H_{rr}^{\text{core}} = \langle \chi_r | \hat{H}^{\text{core}} | \chi_r \rangle, \text{ the core integral}$$

$$\text{and } \gamma_{rs} = \langle \chi_r(1) \chi_s(2) | \frac{e^2}{r_{12}} | \chi_r(1) \chi_s(2) \rangle, \text{ the coulomb repulsion}$$

integral.  $\{\chi_r\}$  belong to the atomic basis set.

Thus, the dependence of  $F_{rr}$  on  $P_{rr}$  allows for the redistribution of charges on all centers as the iterative cycle leading to the self-consistent field progresses. However, this aspect is absent in the simple Hückel representation in that all the diagonal hamiltonian matrix elements,  $H_{rr}^{\dagger}$ , are equal for all atoms. Even if the matrix elements,  $H_{rr}$ , are different, there is no technique inherent in this available for bringing about the charge redistribution. Therefore, a possible improvement on the Hückel approach is to modify each diagonal matrix element of the Hückel matrix in an iterative manner such that it takes into consideration the charge density at that center. This idea was originally proposed by Wheland and Mann<sup>11</sup> and later developed by Streitwieser and Streitwieser and Nair.<sup>12</sup> This charge-dependent procedure, also called the  $\omega$ -technique, is described by the following equation

$$(n)H_{rr} = (n-1)H_{rr} + \omega(1 - (n-1)P_{rr}) \quad (2-2)^{11-13}$$

---

<sup>†</sup>  $H_{rr} = \langle \chi_r | \hat{H}_{\text{eff.}} | \chi_r \rangle$  where  $|\chi_r\rangle$  are the atomic orbital (A.O.) basis and  $\hat{H}_{\text{eff.}}$  is the effective one-particle hamiltonian.

$\omega$  is the perturbation parameter and  $P_{rr}$  is the charge-density on a particular center  $r$ . The subscript  $n$  indicates the order of iteration. Several modifications of this equation<sup>14</sup> have been suggested and yet basically all these methods involve the principle indicated in equation (2-2).

The charge-dependent method has been quite widely used to obtain a better representation of the distribution of charges in many pi-electron systems, radicals, cations, anions and heteronuclear compounds.<sup>12</sup> An examination of the convergence of this method has been carried out.<sup>13</sup> For the allyl and benzyl radicals, a slow oscillatory convergence was noticed.<sup>12</sup> Recently, modifications of this method to remove the oscillations and hasten the convergence have been suggested.<sup>14</sup>

Similar to the charge-dependent methods, we could envisage the bond-order dependent methods, the nature of which is delineated in the next section.

#### 2.202: The Bond-Order Dependent Method

##### 2.2021: The Description

It is generally accepted that there is a relation between the separation,  $R_{rs}$ , between two  $\pi$ -centers  $r$  and  $s$  in a pi-electron system and the so-called pi-electron bond order,  $P_{rs}$ . Such relations have been proposed in the past by Coulson and Golebiewski<sup>15</sup> and others.<sup>16</sup> Although their applicability is

considerable, it is limited in that the equations can only be used for certain classes of molecules, viz., linear polyenes, alternant and non-alternant hydrocarbons. Further, the accuracy of the resulting bond lengths would still depend on the accuracy of the calculated bond order elements. This amounts to seeking better solutions and hence better  $P_{rs}$  with the approximate schemes available. Though one of the schemes, the Pariser-Parr-Pople (PPP) scheme without modification is ubiquitous in its applications for the electronic properties of the  $\pi$ -electron systems, it frequently does not give  $P_{rs}$  which yield sufficiently accurate values of the bond lengths. Consequently, modifications of the basic SCF calculations have been suggested. The most natural modification is a re-evaluation of the basic integrals to adjust for changes in bond lengths. This  $R_{rs}$  dependence can be accounted for by allowing for a dependence of the integrals on the elements of density matrix. As such, the procedure would be second order in  $P_{rs}$ , and although a more accurate representation would be complicated. Rather than go this route we have attempted to modify the first order  $P_{rs}$  dependence of the matrix.<sup>†</sup>

In the bond-order dependent iterative method,<sup>15,16</sup> the variation of the off-diagonal core elements with each iteration is

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<sup>†</sup> Both the core integrals and the coulomb repulsion integrals which constitute the off-diagonal Fock matrix element are assumed to be dependent on the bond order elements through a multiplicative factor.

such that the matrix elements are related to the bond lengths for which new matrix elements are sought. Although a variety of such iterative methods have been suggested, they differ only in the form of the equations used, and the resulting solutions do not differ in content.

## 2.2022: The Delta Technique

The iterative Hückel treatment which is easy to carry out is one of the better known of the techniques for calculating bond lengths. In this simple iterative procedure, the off-diagonal matrix elements,  $H_{rs}$ , are recalculated either from the bond order matrix elements,  $P_{rs}$ , directly or from the bond lengths ( $R_{rs}$ ). To carry out the latter step, a bond length-bond order relation is necessary. For example, Coulson and Golebiewski<sup>15</sup> used Salem's relation<sup>16</sup>

$$({}_n)H_{rs} = ({}_0)H_{rs} \exp \left( -({}_{n-1})(R_{rs} - R_{std})/0.3106 \right) \quad (2-3)$$

along with a bond length-bond order relation

$$({}_{n-1})R_{rs} = 1.517 - 0.18 ({}_{n-1})P_{rs} \quad (2-4)$$

Dewar and Schmeising<sup>21</sup> noted that the equation (2-3), though successful for one class of molecules (viz., alternant aromatic hydrocarbons), does not yield results in agreement with the experimental results for another class (viz., linear polyenes). Therefore, they suggested an alternative expression:

$${}_{(n-1)}R_{rs} = 1.485 - 0.20 {}_{(n-1)}P_{rs} \quad (2-5)$$

for the latter class of molecules.

As is evident now, the lack of flexibility inherent in equations (2-3) and (2-4) or (2-5) limits applicability of this procedure. To get around this difficulty, an iterative procedure has been developed<sup>17</sup> in which the bond length-bond order relation remains the same for all classes of molecules. On the other hand, it does modify the equation for the new matrix element. The form of the new equation for the off-diagonal matrix element is

$${}_{(n)}H_{rs} = {}_{(0)}H_{rs} + \delta ({}_{(n-1)}P_{rs} - P_{std}) \quad (2-6)$$

This relation recognizes the variation in the bond order matrix elements from iteration to iteration through a perturbation on the off-diagonal elements which is proportional to the bond order times  $\delta$ .

The value of the parameter  $\delta$  may be changed from one class of molecules (linear polyenes) to another (polycyclic alternant hydrocarbons) to allow for rapid convergence to accurate values of bond lengths. In practice, it is noticed that the class of molecules, alternant hydrocarbons, where extensive delocalization is discernible, requires a smaller value of  $\delta$  to obtain the bond lengths in agreement with the experiment and for the class of compounds where the phenomenon of delocalization is less predominant, a higher value of  $\delta$  is necessary.<sup>17</sup> Further discussion on this will follow in the succeeding chapters.

Even though the choice of  $\delta$  is fully decided by the type of

molecular system in question, we still have to ask ourselves if there is, indeed, any limitation on the choice of  $\delta$ . Furthermore, any iterative procedure including the one we suggested needs to be checked for convergence. These points are investigated in the following chapter.

## 2.2023: Comments on the $\delta$ Technique and the SCF Treatment

We would like to point out the relation between the present iterative method and the "restricted" SCF-ZDO scheme.<sup>22,23</sup> (Restricted in the sense that the non-neighbour coulomb repulsion integrals are excluded.)

The Fock matrix elements within this SCF-ZDO approximation are given by

$$F_{rr} = U_{rr} + \frac{1}{2} P_{rr} \langle rr | \hat{v} | rr \rangle + \sum_{s(\neq r)} (P_{ss} - 1) \langle rs | \hat{v} | rs \rangle \quad (2-7)$$

$$F_{rs} = \bar{H}_{rs} - \frac{1}{2} P_{rs} \langle rs | \hat{v} | rs \rangle, \text{ } r \text{ and } s \text{ neighbours} \quad (2-8)$$

where  $U_{rr}$  is the diagonal matrix element of  $\chi_r$  with respect to the one-electron hamiltonian and contains the kinetic energy and the interaction with the core of atom  $r$ .  $\bar{H}_{rs}$  is the matrix element of the one-electron hamiltonian for motion in the field of the two nuclei.  $\langle rs | \hat{v} | rs \rangle$  are the two electron repulsion integrals.

For alternant hydrocarbons, these elements reduce to

$$F_{rr} = U_{rr} + \frac{1}{2} \langle rr | \hat{v} | rr \rangle \quad (2-9)$$

and

$$F_{rs} = \bar{H}_{rs} - \frac{1}{2} P_{rs} \langle rs | \hat{v} | rs \rangle \quad (2-10)$$

Now recall that the iterative Hückel scheme defined earlier is characterized by the equations:

$$H_{rr} = \alpha \quad \text{and} \quad H_{rs} = H'_{rs} + \delta P_{rs} \quad (2-11)$$

where

$$H'_{rs} = \left( (0)H_{rs} - \delta P_{std} \right) = \left( \beta^0 - \delta P_{std} \right)$$

On assuming that the non-neighbour interactions for the repulsion integrals are zero, the present iterative method and the SCF-ZDO scheme become equivalent except that the elements have a somewhat different interpretation.

In the case of alternant hydrocarbons the variation of the off-diagonal element will have no effect on the diagonal matrix elements of the density matrix.<sup>23</sup> This implies that for a given geometry of the system,  $F_{rr}$  is iteration independent. This is to be compared to  $H_{rr}$  remaining the same at all stages of our iterative procedure. The elements that change then are the off-diagonal Fock matrix element in SCF-ZDO and  $H_{rs}$ , the off-diagonal Hückel matrix element, in our approach. In the former case, this change comes through the exchange term



$-\frac{1}{2} P_{rs} \langle rs | \hat{v} | rs \rangle$  and in the latter through  $\delta P_{rs}$ . Clearly, for the fixed geometry model,  $\langle rs | \hat{v} | rs \rangle$  remains the same at all stages of the iteration. However,  $P_{rs}$  varies. Similarly,  $\delta$  remains the same; it is again  $P_{rs}$  that changes. In the procedure that we carried out, a constant term  $(-\delta)$  is added to  $(0)H_{rs} = \beta^0$  to give  $H'_{rs}$ ; this is an initial perturbation which of course remains the same throughout the iteration procedure. Since  $\delta$  may take different values for different classes of alternants, this allows us to introduce different  $H'_{rs}$  for the different classes while at the same time maintaining the one parameter character of our procedure.

From the point of view of a self-consistent field procedure in  $P_{rs}$  the matrix element  $H'_{rs}$  defines the initial energy. The energy obtained after  $n$  iterations is decreased from this value (although increased from the "unperturbed" energy defined by  $(0)H_{rs}$ ). In order to make contact with the more common iterative procedures (the procedures by Longuet-Higgins and Salem,<sup>16</sup> Coulson and Golebiewski<sup>15</sup>) and to enable us to develop a perturbation treatment, we take  $H_{rs}$  and not  $H'_{rs}$  as the zero order element and  $\delta (P_{rs} - P_{std})$  as the perturbation in the iterative self-consistent procedure.

As one goes from the alternants to the non-alternants, a difficulty arises. While the SCF-ZDO scheme yields self-consistent results in the charge-distribution, the  $\delta$  technique does not consider this aspect explicitly. As we shall see, for

the purpose of bond length calculations, an appropriate choice of  $\delta$  appears to take this into consideration in an adequate manner.

## CHAPTER 3

### THE ITERATIVE ANALYSIS

#### 3.10: INTRODUCTION

The iterative analysis that will be delineated in this chapter, as we shall see, follows the perturbation theoretic approach based on an independent particle model. Since in the course of the analysis, references will be made to the existing approaches, a brief outline of the perturbation theories germane to the present problem is given in the following. Succeeding this, a formulation of our approach is presented.

Coulson and Longuet-Higgins<sup>24</sup> and Longuet-Higgins<sup>25</sup> introduced the perturbation theory based on an independent particle model to consider the effect of varying the coulomb integral,  $H_{rr}$ , or the bond integral,  $H_{rs}$ , on the total  $\pi$ -electron energy,  $E_{\pi}$  and the bond order matrix elements  $P_{rs}$ . Their procedure was further developed by Dewar<sup>26</sup> and extensively used to study the electronic spectra and chemical reactivities of the molecules containing  $\pi$ -electron systems by several others.<sup>27</sup>

Recently, Imamura<sup>28</sup> and Carbo<sup>29</sup> gave a general perturbation theory for the extended Hückel scheme. McWeeny<sup>30</sup> presented the matrix formulation for the self-consistent field perturbation theory. The McWeeny density matrix formulation allows one to go to any order of perturbation. Further, the perturbations are not confined to one element of the hamiltonian matrix. In all these treatments, one-particle

perturbations are considered. Very recently, Sustmann and Binsch extended the self-consistent perturbation theory for two interacting closed-shell molecules where the one- and two-particle perturbations are important.<sup>31</sup>

### 3.20: THE ITERATIVE ANALYSIS

#### 3.201: Formulation

For any pi-electron system, if the variation of the orbital coefficients between two successive iterations is known, then it would be possible to follow the process from iteration to iteration. However, a knowledge of the effect of the variation is difficult to achieve for most of the pi-electron systems. To surmount this difficulty, an attempt was made to obtain the first order orbital coefficients for the first iterated secular equation using the Rayleigh-Schrödinger perturbation theory. Assuming that the Rayleigh-Schrödinger perturbation treatment leads to a very fast convergent result for the given problem, we truncated the perturbation expansion only to first order terms. Even though truncating to a first order term may be a serious mistake, since the interest lies in establishing how the orbital coefficients are related to a first order approximation, the results obtained will probably act as guidelines in examining the convergence. Once the first iterated secular equation is solved, the second iterated secular equation is set up for which the same procedure is followed. With the algebraic equations available for the coefficients, after a detailed derivation, the analysis is carried out. In the following, we derive the appropriate equations

and then discuss the implications of our results.

The equations to be solved are:

$$\sum_s \left( (1)_{rs}^{H} - \delta_{rs} E_i \right) C_{si} = 0; \quad r = 1, 2, \dots, n \quad (3-1)^{\dagger}$$

Equation (3-1) is the first iterated secular equation where  $(1)_{rs}^{H}$  are the hamiltonian matrix elements expressed as

$$(1)_{rs}^{H} = (0)_{rs}^{H(0)} + \delta_{(0)}^{(1)} H_{rs} \quad (3-2)$$

The nature of the perturbation is described in section 3.203. The subscript on the left refers to the number of iterations and the superscript on the right refers to the order of the term.  $\delta_{rs}$  is the Kronecker delta.  $C_{si}$  are orbital coefficients. Since the perturbation expansion will be truncated at first order terms, one has:

$$(n)_{rs}^{H} = (0)_{rs}^{H(0)} + \delta_{(n-1)}^{(1)} H_{rs} \quad (3-3)$$

$$(n)_{i}^{E} = (0)_{i}^{E(0)} + \delta_{(n-1)}^{(1)} E_i \quad (3-4)$$

$$(n)_{ri}^{C} = (0)_{ri}^{C(0)} + \delta_{(n-1)}^{(1)} C_{ri} \quad (3-5)$$

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†

See reference 22 for derivation.

In Chapters 3 and 4, a multiplicative factor 2 should be included in the definition of the zeroth order and higher order bond order elements, P.

where  $\delta$  is the perturbation parameter. The perturbed atomic orbital coefficient of each molecular orbital can be expanded in the way indicated in equation (3-5). Substituting for  $(1)H_{rs}$ ,  $(1)E_i$  and  $(1)C_{si}$  in equation (3-1) and picking up the terms which appear as coefficients to each power of perturbation would yield

$$\sum_s \left( H_{rs}^{(0)} - \delta_{rs} E_i^{(0)} \right) C_{si}^{(0)} = 0; \quad (r = 1, 2, \dots, n) \quad (3-6)$$

$$\begin{aligned} & \sum_s \left( H_{rs}^{(1)} - \delta_{rs} E_i^{(1)} \right) C_{si}^{(0)} + \\ & \sum_s \left( H_{rs}^{(0)} - \delta_{rs} E_i^{(0)} \right) C_{si}^{(1)} = 0; \quad (r = 1, 2, \dots, n) \end{aligned} \quad (3-7)$$

Since the zeroth order molecular orbitals are normalised,

$$\sum_r \sum_s \delta_{rs} C_{ri}^{(0)} C_{si}^{(0)} = 1 \quad (3-8)$$

The expression for  $E_i^{(1)}$  can then be written as

$$E_i^{(1)} = \sum_r \sum_s H_{rs}^{(1)} C_{ri}^{(0)} C_{si}^{(0)} \quad (3-9)$$

To obtain the correction to the orbital coefficient one first multiplies (3-7) by  $C_{rj}^{(0)}$ , and then, on carrying out the summation over all  $r$ , and recognizing that

$$\sum_r \sum_s \delta_{rs} C_{ri}^{(0)} C_{sj}^{(0)} = 0 \quad (3-10)$$

we obtain:

$$\sum_r \sum_s \delta_{rs} C_{rj}^{(0)} C_{si}^{(1)} = - \left( 1 / (E_j^{(0)} - E_i^{(0)}) \right) x$$

$$\sum_r \sum_s H_{rs}^{(1)} C_{ri}^{(0)} C_{sj}^{(0)} \quad (3-11)$$

Multiplying the above equation by  $C_{pj}^{(0)}$  and summing over all  $j$  except  $i$  of the resulting equation gives rise to

$$\sum_j C_{pj}^{(0)} \sum_r \sum_s \delta_{rs} C_{rj}^{(0)} C_{si}^{(1)} - C_{pi}^{(0)} \sum_r \sum_s \delta_{rs} C_{ri}^{(0)} C_{si}^{(1)}$$

$$\equiv - \sum_{j \neq i} \sum_r \sum_s \left( H_{rs}^{(1)} / [E_j^{(0)} - E_i^{(0)}] \right) C_{ri}^{(0)} C_{sj}^{(0)} C_{pj}^{(0)} \quad (3-12)$$

In order to simplify equation (3-12), we need relations between the  $C_{ri}^{(0)}, C_{sj}^{(0)}, C_{pj}^{(0)}$  etc. To this end, we express the perturbed molecular orbitals in terms of the initial basis set as

$$|\psi_i\rangle = \sum_r C_{ri} |\phi_r\rangle \quad (3-13)$$

$$|\psi_j\rangle = \sum_s C_{sj} |\phi_s\rangle \quad (3-14)$$

Treating  $C_{ri}$  as the real coefficients and using (3-5), we obtain

$$\langle \psi_i | \psi_j \rangle \equiv \delta_{ij} \cong \sum_r \sum_s C_{ri}^{(0)} C_{sj}^{(0)} \langle \phi_r | \phi_s \rangle$$

$$+ \delta \sum_r \sum_s C_{ri}^{(0)} C_{sj}^{(1)} \langle \phi_r | \phi_s \rangle +$$



$$\delta \sum_r \sum_s c_{ri}^{(1)} c_{sj}^{(0)} \langle \phi_r | \phi_s \rangle$$

All the higher order terms in  $\delta$  are neglected. Using the neglect of overlap approximation, we obtain

$$\sum_r \sum_s c_{ri}^{(0)} c_{si}^{(0)} \delta_{rs} + 2\delta \sum_r \sum_s c_{ri}^{(0)} c_{si}^{(1)} \delta_{rs} \approx 1 \quad (3-15)$$

Hence, to a first order approximation,

$$2\delta \sum_r \sum_s c_{ri}^{(0)} c_{si}^{(1)} \delta_{rs} \approx 0 \quad (3-16)$$

Substituting (3-16) into (3-12) and considering

$$\sum_r c_{ri}^{(0)} c_{rj}^{(0)} = \delta_{ij} \quad (3-17)$$

$$\text{and } \sum_j \sum_p c_{rj}^{(0)} c_{pj}^{(0)} \delta_{sp} = \delta_{rs} \quad (3-18)$$

we get, after some rearrangement

$$c_{pi}^{(1)} = \sum_{j \neq i} \left( c_{pj}^{(0)} / (E_i^{(0)} - E_j^{(0)}) \right) \sum_r \sum_s H_{rs}^{(1)} c_{ri}^{(0)} c_{sj}^{(0)} \quad (3-19)$$

$${}^{(0)}\Delta E_j^i = (E_j^{(0)} - E_i^{(0)}) \quad \text{and} \quad {}^{(0)}\Delta E_i^j = (E_i^{(0)} - E_j^{(0)})$$

will be used subsequently.

### 3.202: The Coupling Phenomenon

The expansion for the matrix element can be written as

$$\begin{aligned}
 {}^{(1)}H_{rs} &= {}^{(0)}H_{rs} + \delta {}^{(0)}H_{rs}^{(1)} \\
 &= {}^{(0)}H_{rs} + \delta \left( \sum_i \eta {}^{(0)}C_{ri} {}^{(0)}C_{si} - 1 \right) \quad (3-20)
 \end{aligned}$$

where  $\eta$  is the occupation number and the  ${}^{(0)}C_{ri}$   ${}^{(0)}C_{si}$  are known for the zeroth order problem. Similarly, the hamiltonian matrix element of the second iteration is:

$$\begin{aligned}
 {}^{(2)}H_{rs} &= {}^{(0)}H_{rs} + \delta {}^{(1)}H_{rs} \\
 &= {}^{(0)}H_{rs} + \delta \left( \sum_i \eta {}^{(1)}C_{ri} {}^{(1)}C_{si} - 1 \right) \quad (3-21)
 \end{aligned}$$

where the coefficients  ${}^{(1)}C_{ri}$  and  ${}^{(1)}C_{si}$  are given by equation (3-5).

Equations (3-20) and (3-21) indicate that the matrix elements for the  $n^{\text{th}}$  iteration are dependent on the perturbation coefficients obtained in the previous iteration. These coefficients are of course dependent on the matrix elements of the  $n-1$  solution, hence the iterations are coupled through the products of orbital coefficients, i.e. through density matrix elements. We shall follow the iteration through the bond order matrix elements.

### 3.203: Generalization

#### 3.2031: An Expression for the Density Matrix

We have earlier obtained the expression for the first iterated solution to a first order accuracy using the perturbation theory as

$$({}_1)C_{ri} = ({}_0)C_{ri}^{(0)} + \delta \sum_{j \neq i} \left( ({}_0)C_{rj}^{(0)} / \Delta E_i^j \right) x$$

$$\sum_p \sum_q ({}_0)H_{pq}^{(1)} ({}_0)C_{pi}^{(0)} ({}_0)C_{qj}^{(0)} \quad (3-22)$$

Neglecting the second order term in  $\delta$  in (3-22) allows one to write the product for  $({}_1)C_{ri} ({}_1)C_{si}$  as:

$$\begin{aligned} ({}_1)C_{ri} ({}_1)C_{si} &\approx ({}_0)C_{ri}^{(0)} ({}_0)C_{si}^{(0)} + \\ &\delta ({}_0)C_{ri}^{(0)} \sum_{j \neq i} \left( ({}_0)C_{sj}^{(0)} / \Delta E_i^j \right) \sum_p \sum_q ({}_0)H_{pq}^{(1)} ({}_0)C_{pi}^{(0)} ({}_0)C_{qj}^{(0)} \\ &+ \delta ({}_0)C_{si}^{(0)} \sum_{j \neq i} \left( ({}_0)C_{rj}^{(0)} / \Delta E_i^j \right) \sum_p \sum_q ({}_0)H_{pq}^{(1)} ({}_0)C_{pi}^{(0)} ({}_0)C_{qj}^{(0)} \end{aligned} \quad (3-23)$$

Summing over all the occupied levels, carrying out an expansion of the resulting expression and rearranging the terms, results in the expression for the first iterated density matrix element:

$$\begin{aligned} ({}_1)P_{rs} &= \sum_{i=1}^{N/2} ({}_1)C_{ri} ({}_1)C_{si} = \sum_i ({}_0)C_{ri}^{(0)} ({}_0)C_{si}^{(0)} \\ &+ \delta \sum_{i=1}^{N/2} \sum_{j=\frac{N}{2}+1}^N \left( ({}_0)C_{ri}^{(0)} ({}_0)C_{sj}^{(0)} + ({}_0)C_{si}^{(0)} ({}_0)C_{rj}^{(0)} \right) x \\ &\sum_{p,q} \left( ({}_0)H_{pq}^{(1)} ({}_0)C_{pi}^{(0)} ({}_0)C_{qj}^{(0)} / ({}_0)\Delta E_i^j \right) \end{aligned} \quad (3-24)$$

McWeeny, and Dierckson and McWeeny<sup>30</sup> using the perturbation theory obtained an expression for the first order correction to the first order density matrix. Our expression can be shown to be equivalent.

Extending this procedure allows us to write the expressions for the second iterated density matrix element and the third iterated density matrix element as

$$\begin{aligned}
 {}^{(2)}P_{rs} = & \sum_{i=1}^{N/2} {}^{(2)}C_{ri} {}^{(2)}C_{si} = \sum_{i=1}^{N/2} {}^{(0)}C_{ri} {}^{(0)}C_{si} \\
 & + \delta \left[ \sum_{i=1}^{N/2} \sum_{j=\frac{N}{2}+1}^N \left( {}^{(0)}C_{ri} {}^{(0)}C_{sj} + {}^{(0)}C_{si} {}^{(0)}C_{rj} \right) x \right. \\
 & \left. \sum_{p,q} \left( {}^{(0)}H_{pq}^{(1)} {}^{(0)}C_{pi} {}^{(0)}C_{qj} / {}^{(0)}\Delta E_i^j \right) \right] + \\
 & \delta^2 \left[ \sum_{i=1}^{N/2} \sum_{j=\frac{N}{2}+1}^N \left( {}^{(0)}C_{ri} {}^{(0)}C_{sj} + {}^{(0)}C_{si} {}^{(0)}C_{rj} \right) \right. \\
 & \left. \left\{ \left\{ \sum_{p,q} \left\{ \sum_m \sum_n \left( {}^{(0)}C_{pm} {}^{(0)}C_{qn} + {}^{(0)}C_{qm} {}^{(0)}C_{pn} \right) x \right. \right. \right. \right. \\
 & \left. \left. \sum_{u,v} \left( {}^{(0)}H_{uv}^{(1)} {}^{(0)}C_{um} {}^{(0)}C_{vn} / {}^{(0)}\Delta E_m^n \right) \right\} x \right. \right. \\
 & \left. \left. {}^{(0)}C_{pi} {}^{(0)}C_{qj} / {}^{(0)}\Delta E_i^j \right\} \right\} \right] \quad (3-25)
 \end{aligned}$$

$$({}_3)P_{rs} = \sum_{i=1}^{N/2} ({}_3)C_{ri} ({}_3)C_{si} = \sum_{i=1}^{N/2} ({}_0)C_{ri}^{(0)} ({}_0)C_{si}^{(0)} +$$

$$\delta \left[ \sum_{i=1}^{N/2} \sum_{j=\frac{N}{2}+1}^N \left( ({}_0)C_{ri}^{(0)} ({}_0)C_{sj}^{(0)} + ({}_0)C_{si}^{(0)} ({}_0)C_{rj}^{(0)} \right) \times \right.$$

$$\left. \left\{ \sum_{p,q}^N \left( ({}_0)H_{pq}^{(1)} ({}_0)C_{pi}^{(0)} ({}_0)C_{qj}^{(0)} \right) / ({}_0)\Delta E_i^j \right\} \right] +$$

$$\delta^2 \left[ \sum_{i=1}^{N/2} \sum_{j=\frac{N}{2}+1}^N \left( ({}_0)C_{ri}^{(0)} ({}_0)C_{sj}^{(0)} + ({}_0)C_{si}^{(0)} ({}_0)C_{rj}^{(0)} \right) \right.$$

$$\left. \left\{ \sum_{p,q}^N \left\{ \sum_{k=1}^{N/2} \sum_{\ell=\frac{N}{2}+1}^N \left( ({}_0)C_{pk}^{(0)} ({}_0)C_{q\ell}^{(0)} + ({}_0)C_{qk}^{(0)} ({}_0)C_{p\ell}^{(0)} \right) \right\} \times \right. \right.$$

$$\left. \sum_{u,v}^N \left( ({}_0)H_{uv}^{(1)} ({}_0)C_{uk}^{(0)} ({}_0)C_{v\ell}^{(0)} / ({}_0)\Delta E_k^\ell \right) \right\} \times$$

$$\left. ({}_0)C_{pi}^{(0)} ({}_0)C_{qj}^{(0)} / ({}_0)\Delta E_i^j \right\} \left\{ \left\{ \left\{ \right\} \right\} \right\} \left. \right]$$

$$+ \delta^3 \left[ \left\{ \sum_{i=1}^{N/2} \sum_{j=\frac{N}{2}+1}^N \left( ({}_0)C_{ri}^{(0)} ({}_0)C_{sj}^{(0)} + ({}_0)C_{si}^{(0)} ({}_0)C_{rj}^{(0)} \right) \right\} \sum_{p,q}^N \right.$$

$$\left. \left\{ \sum_k^{N/2} \sum_\ell^N \left( ({}_0)C_{pk}^{(0)} ({}_0)C_{q\ell}^{(0)} + ({}_0)C_{qk}^{(0)} ({}_0)C_{p\ell}^{(0)} \right) \right\} \sum_{t,w}^N \left\{ \sum_{m=1}^{N/2} \sum_{n=\frac{N}{2}+1}^N \right. \right.$$

$$\begin{aligned}
 & \left( (0)C_{tm}^{(0)} (0)C_{wn}^{(0)} + (0)C_{tn}^{(0)} (0)C_{wm}^{(0)} \right) \\
 & \sum_{u,v} \left\{ (0)H_{uv}^{(1)} (0)C_{um}^{(0)} (0)C_{vn}^{(0)} / (0)\Delta E_m^n \right\} (0)C_{tk}^{(0)} (0)C_{wl}^{(0)} / \\
 & (0)\Delta E_k^l \left\{ (0)C_{pi}^{(0)} (0)C_{qj}^{(0)} / (0)\Delta E_i^j \right\} \Bigg] \quad (3-26)
 \end{aligned}$$

### 3.2032: The Condensation Procedure

Because of the unwieldy nature of (3-24), (3-25) and (3-26), we have resorted to using a condensed form for which the following notation is used. Previously, i, j, k, l, m, n... denoted the subscripts for the molecular orbitals; p, q, r, s, t, u, v, w... the subscripts for the centers. As the centers and the M.O.'s occur in pairs, a notation pertaining to the pair (pair of M.O.'s or pair of centers) is used. Thus, for the molecular orbital pairs I, J, K, L, M, N... symbols are used. P, Q, R, S, T... represent the paired centers. In the following, we will demonstrate how the condensed forms are obtained for the corrections to the first, second and third iterated density matrix elements.

First, noting that

$$\begin{aligned}
 & \sum_p \sum_q \left( (0)C_{pi}^{(0)} (0)C_{qj}^{(0)} E_{ij}^{-1} (0)H_{pq}^{(1)} \right) \\
 & = \sum_p \sum_q \left( \left( (0)C_{pi}^{(0)} (0)C_{qj}^{(0)} E_{ij}^{-1} / 2 \right) + \right.
 \end{aligned}$$

$$\left( (0)C_{pj}^{(0)} (0)C_{qi}^{(0)} E_{ij}^{-1} / 2 \right) (0)H_{pq}^{(1)} \quad (3-27)$$

where  $E_{ij}^{-1} = \Delta E_i^j$  and replacing  $E_{ij}^{-1} / 2 = E_{ij}$  without loss of generality, the correction to the first iterated density matrix element as given by the second term in equation (3-24) is rewritten as

$$\begin{aligned} (1)P_{rs}^{(1)} &= \delta \sum_{i=1}^{N/2} \sum_{j=\frac{N}{2}+1}^N \left( (0)C_{ri}^{(0)} (0)C_{sj}^{(0)} + (0)C_{si}^{(0)} (0)C_{rj}^{(0)} \right) \times \\ &\quad \sum_p \sum_q \left( (0)H_{pq}^{(1)} (0)C_{pi}^{(0)} (0)C_{qj}^{(0)} / \Delta E_i^j \right) \\ &= \delta \sum_{i,j} \sum_{p,q} \left( (0)A_{rs,ij} E_{ij} (0)A_{pq,ij} \right) (0)H_{pq}^{(1)} \end{aligned} \quad (3-28)$$

where  $(0)A_{rs,ij} = \left( (0)C_{ri}^{(0)} (0)C_{sj}^{(0)} + (0)C_{si}^{(0)} (0)C_{rj}^{(0)} \right)$ .

On using the 'pair-notation' defined earlier, equation (3-28) becomes

$$(1)P_T^{(1)} = \delta \sum_I \sum_Q \left( (0)A_{TI} (0)E_I (0)A_{QI} \right) (0)H_Q^{(1)} \quad (3-29)$$

where  $(0)A_{TI} = (0)A_{rs,ij}$

Similarly, the corrections to the second and third iterated density matrix elements as given in equation (3-25) or equation (3-26), are written in the condensed form as

$$\begin{aligned}
 {}^{(2)}P_T^{(1)} = & \delta \sum_I \sum_Q \left( (0)A_{TI} E_I (0)A_{QI} \right) (0)H_Q^{(1)} \\
 & + \delta^2 \sum_I \sum_Q \sum_J \sum_R \left( (0)A_{TI} E_I (0)A_{QI} \right) \left( (0)A_{QJ} E_J (0)A_{RJ} \right) (0)H_R^{(1)}
 \end{aligned}
 \tag{3-30}$$

and

$$\begin{aligned}
 {}^{(3)}P_T^{(1)} = & \delta \sum_{I,Q} \left( (0)A_{TI} E_I (0)A_{QI} \right) (0)H_Q^{(1)} \\
 & + \delta^2 \sum_I \sum_Q \sum_J \sum_R \left( (0)A_{TI} E_I (0)A_{QI} \right) \left( (0)A_{QJ} E_J (0)A_{RJ} \right) (0)H_R^{(1)} \\
 & + \delta^3 \sum_I \sum_Q \sum_J \sum_R \sum_K \sum_S \left( (0)A_{TI} E_I (0)A_{QI} \right) \left( (0)A_{QJ} E_J (0)A_{RJ} \right) \\
 & \left( (0)A_{RK} E_K (0)A_{SK} \right) (0)H_S^{(1)}
 \end{aligned}
 \tag{3-31}$$

For a closed-shell N-electron problem, in general, the summation indices I, J, K, L... run over  $(N/2)^2$  values and P, Q, R, S... run over  $N^2$  values. Recognizing this allows equations (3-29), (3-30) and (3-31) to be written as

$${}^{(1)}P_T^{(1)} = \delta \sum_{I,Q} \left( A_{TI} E_I A_{IQ}^\dagger \right) (0)H_Q^{(1)}
 \tag{3-32}$$



$$\begin{aligned}
 {}_{(2)}P_T^{(1)} = & \delta \sum_{I,Q} A_{TI} E_I A_{IQ}^\dagger {}_{(0)}H_Q^{(1)} + \delta^2 \sum_{I,Q,J,R} \left( A_{TI} E_I A_{IQ}^\dagger \right) \\
 & \left( A_{QJ} E_J A_{JR}^\dagger \right) {}_{(0)}H_R^{(1)} \quad (3-33)
 \end{aligned}$$

and

$$\begin{aligned}
 {}_{(3)}P_T^{(1)} = & \delta \sum_{I,Q} A_{TI} E_I A_{IQ}^\dagger {}_{(0)}H_Q^{(1)} + \delta^2 \sum_{I,Q,J,R} \left( A_{TI} E_I A_{IQ}^\dagger \right) \\
 & \left( A_{QJ} E_J A_{JR}^\dagger \right) {}_{(0)}H_R^{(1)} + \delta^3 \sum_{I,Q,J,R,K,S} \left( A_{TI} E_I A_{IQ}^\dagger \right) \\
 & \left( A_{QJ} E_J A_{JR}^\dagger \right) \left( A_{RK} E_K A_{KS}^\dagger \right) {}_{(0)}H_S^{(1)} \quad (3-34)
 \end{aligned}$$

Since the transpose of IQ element of A is  $A_{QI}$ , we replaced  $A_{QI}$  by  $A_{IQ}^\dagger$  in the above equations. In this notation, the density matrix element for a pair T (a pair of centers) at the end of the first iteration to a first order approximation is given by

$${}_{(1)}P_T \simeq {}_{(0)}P_T^{(0)} + \delta {}_{(0)}P_T^{(1)} \quad (3-35)$$

$$\simeq {}_{(0)}P_T^{(0)} + \delta {}_{(0)}(\underline{A} \quad \underline{B} \quad \underline{H})_T \quad (3-36)$$

where  $\underline{B} = \underline{E} \underline{A}^\dagger$ .

Similarly,

$$\begin{aligned}
 {}_{(2)}\mathbf{P}_T &\approx {}_{(0)}\mathbf{P}_T^{(0)} + \delta {}_{(0)}\mathbf{P}_T^{(1)} + \delta^2 {}_{(0)}\mathbf{P}_T^{(2)} \\
 &\approx {}_{(0)}\mathbf{P}_T^{(0)} + \delta {}_{(0)}(\underline{A} \underline{B} \underline{H})_T + \delta^2 {}_{(0)}(\underline{A} \underline{B} \underline{A} \underline{B} \underline{H})_T \quad (3-37)
 \end{aligned}$$

$$\begin{aligned}
 {}_{(3)}\mathbf{P}_T &\approx {}_{(0)}\mathbf{P}_T^{(0)} + \delta {}_{(0)}(\underline{A} \underline{B} \underline{H})_T + \delta^2 {}_{(0)}(\underline{A} \underline{B} \underline{A} \underline{B} \underline{H})_T + \\
 &\delta^3 {}_{(0)}(\underline{A} \underline{B} \underline{A} \underline{B} \underline{A} \underline{B} \underline{H})_T \quad (3-38)
 \end{aligned}$$

$$\begin{aligned}
 {}_{(n)}\mathbf{P}_T &\approx {}_{(0)}\mathbf{P}_T^{(0)} + \delta {}_{(0)}(\underline{A} \underline{B} \underline{H})_T \\
 &+ \delta^2 {}_{(0)}(\underline{A} \underline{B} \underline{A} \underline{B} \underline{H})_T + \cdots + \delta^n {}_{(0)}(\underline{A} \underline{B} (\underline{A} \underline{B})^{n-1} \underline{H})_T \quad (3-39)
 \end{aligned}$$

Recalling equation (3-3) that at each stage of the iteration, the new hamiltonian matrix element is obtained from an expression for  $(\mathbf{P}_T - \mathbf{P}_{\text{std}})$ . Subtracting  $\mathbf{P}_{\text{std}}$  from both sides of equations (3-36), (3-37), (3-38) and (3-39) gives the  $n^{\text{th}}$  iterated expression for  $(\mathbf{P}_T - \mathbf{P}_{\text{std}})$  as  ${}_{(n)}(\mathbf{P}_T - \mathbf{P}_{\text{std}}) = {}_{(n)}\Delta\mathbf{P}_T$

$$\begin{aligned}
 &= {}_{(0)}\Delta\mathbf{P}_T + \delta {}_{(0)}(\underline{A} \underline{B} \underline{H})_T + \delta^2 {}_{(0)}(\underline{A} \underline{B} \underline{A} \underline{B} \underline{H})_T + \cdots + \\
 &\delta^n {}_{(0)}(\underline{A} \underline{B} (\underline{A} \underline{B})^{n-1} \underline{H})_T \quad (3-40)
 \end{aligned}$$

When all the pairs of the centers are considered, the  $n^{\text{th}}$  iterated density matrix and also the matrix made up of  ${}_n\Delta \mathbf{P}_T$  could be cast into a column vector. Thus, the final form of the column vector made up of  $\mathbf{P}_T$ 's is

$$({}_n)\underline{\mathbf{P}} \approx ({}_0)\underline{\mathbf{P}}^{(0)} + \delta \underline{\mathbf{P}}^{(1)} + \delta^2 \underline{\mathbf{P}}^{(2)} + \dots + \delta^n \underline{\mathbf{P}}^{(n)} \quad (3-41)$$

$$\approx ({}_0)\underline{\mathbf{P}}^{(0)} + ({}_0)\left\{ \sum_{n=1} (\delta \underline{\mathbf{A}} \underline{\mathbf{B}})^n \right\} ({}_0)\underline{\mathbf{H}}^{(1)} \quad (3-42)$$

where

$$({}_n)\underline{\mathbf{P}} = \begin{bmatrix} \mathbf{P}_1 \\ \mathbf{P}_2 \\ \mathbf{P}_N \end{bmatrix}$$

Correspondingly,

$$({}_n)\Delta \underline{\mathbf{P}} = ({}_0)\Delta \underline{\mathbf{P}}^{(1)} + \left\{ \sum_{n=1} (\delta \underline{\mathbf{A}} \underline{\mathbf{B}})^n \right\} ({}_0)\underline{\mathbf{H}}^{(1)} \quad (3-43)$$

From (3-36), it is clear that  $\underline{\mathbf{A}} \underline{\mathbf{B}} = \underline{\mathbf{A}} \underline{\mathbf{E}} \underline{\mathbf{A}}^\dagger$  where  $\underline{\mathbf{E}}$  is the diagonal matrix. Substituting  $\underline{\mathbf{A}} \underline{\mathbf{B}} = \underline{\mathbf{A}} \underline{\mathbf{E}} \underline{\mathbf{A}}^\dagger$  into (3-42) and (3-43) and recognizing  $({}_0)\underline{\mathbf{H}}^{(1)}$  with  $({}_0)\Delta \underline{\mathbf{P}}^{(1)}$ , one could write (3-42) and (3-43) respectively as

$$({}_n)\underline{\mathbf{P}} \approx ({}_0)\underline{\mathbf{P}}^{(0)} + ({}_0)\left\{ \sum_{n=1} (\delta \underline{\mathbf{A}} \underline{\mathbf{E}} \underline{\mathbf{A}}^\dagger)^n \right\} ({}_0)\Delta \underline{\mathbf{P}}^{(1)} \quad (3-44)$$

and

$${}_{(n)}\Delta \underline{\underline{\mathbf{P}}} \approx {}_{(0)}\Delta \underline{\underline{\mathbf{P}}}^{(1)} + {}_{(0)}\left\{ \sum_{n=1} (\delta \underline{\underline{\mathbf{A}}} \underline{\underline{\mathbf{E}}} \underline{\underline{\mathbf{A}}}^{\dagger})^n \right\} {}_{(0)}\Delta \underline{\underline{\mathbf{P}}}^{(1)} \quad (3-45)$$

### 3.2033: The Convergence Criterion

Having obtained expressions for  ${}_{(n)}\underline{\underline{\mathbf{P}}}$  and  ${}_{(n)}\Delta \underline{\underline{\mathbf{P}}}$ , one can carry out the test for convergence. To do so, the relation for  ${}_{(n)}\Delta \underline{\underline{\mathbf{P}}}$  given by (3-45) is rewritten as

$${}_{(n)}\Delta \underline{\underline{\mathbf{P}}} \approx {}_{(0)}\Delta \underline{\underline{\mathbf{P}}}^{(1)} + \left\{ \delta \underline{\underline{\mathbf{A}}} \underline{\underline{\mathbf{E}}} \underline{\underline{\mathbf{A}}}^{\dagger} \right\} {}_{(0)}\left\{ \sum_{n=0} (\delta \underline{\underline{\mathbf{A}}} \underline{\underline{\mathbf{E}}} \underline{\underline{\mathbf{A}}}^{\dagger})^{n-1} \right\} \times {}_{(0)}\Delta \underline{\underline{\mathbf{P}}}^{(1)} \quad (3-46)$$

Clearly,  $\sum_{n=0} (\delta \underline{\underline{\mathbf{A}}} \underline{\underline{\mathbf{E}}} \underline{\underline{\mathbf{A}}}^{\dagger})^{n-1}$  represents a geometric series. It will be a converging series provided the eigenvalues of the matrix  $(\delta \underline{\underline{\mathbf{A}}} \underline{\underline{\mathbf{E}}} \underline{\underline{\mathbf{A}}}^{\dagger})$  are less than unity.<sup>34</sup> For the eigenvalues less than unity, as  $n \rightarrow \infty$ ,

$${}_{(n)}\Delta \underline{\underline{\mathbf{P}}} \approx {}_{(0)}\Delta \underline{\underline{\mathbf{P}}}^{(1)} + \left\{ \delta \underline{\underline{\mathbf{A}}} \underline{\underline{\mathbf{E}}} \underline{\underline{\mathbf{A}}}^{\dagger} \right\} \left\{ \underline{\underline{\mathbf{1}}} - \delta \underline{\underline{\mathbf{A}}} \underline{\underline{\mathbf{E}}} \underline{\underline{\mathbf{A}}}^{\dagger} \right\}^{-1} {}_{(0)}\Delta \underline{\underline{\mathbf{P}}}^{(1)} \quad (3-47)$$

Since  $(\delta \underline{\underline{\mathbf{A}}} \underline{\underline{\mathbf{E}}} \underline{\underline{\mathbf{A}}}^{\dagger})$  and  $(\underline{\underline{\mathbf{1}}} - \delta \underline{\underline{\mathbf{A}}} \underline{\underline{\mathbf{E}}} \underline{\underline{\mathbf{A}}}^{\dagger})^{-1}$  commute, equation (3-47) yields

$${}_{(n)}\Delta\mathbf{P} = (\underline{1} - \delta \underline{A} \underline{B})^{-1} {}_{(0)}\Delta\mathbf{P}^{(1)} \quad (3-48)$$

The final closed form expression for  ${}_{(n)}\Delta\mathbf{P}$  is valid for the linear relation used in the  $\delta$  technique (equation 2-6 ). It is equally valid for the truncated form of Salem's relation (equation 2-3 ) at the first order, after substituting into this equation the Coulson-Golebiewski bond length-bond order relation.<sup>15</sup>

### 3.30: CONVERGENCE

#### 3.301: The Eigenvalues of the Supermatrix, $\delta \underline{A} \underline{E} \underline{A}^\dagger$

It can be readily shown that the eigenvalues  $\lambda$  for the supermatrix  $\underline{A} \underline{E} \underline{A}^\dagger$  are linearly related to those ( $\lambda_p$ ) of the polarizability matrix ( $\underline{\pi}_p$ ) as  $\lambda = \lambda_p/2$ . Hence the eigenvalues of  $\delta \underline{A} \underline{E} \underline{A}$  are given by  $\lambda_\delta = \lambda_p/2_\delta$ . Binsch et al<sup>32</sup> have obtained the eigenvalues  $\lambda_p$  for many of the systems of interest to us (e.g. condensed cyclic polyenes, linear polyenes, selected non-alternants - see Chapter 6), and for reference, pertinent  $\lambda_p$  values are displayed in Table 3.1. Consideration of these values indicates that, except for special cases, e.g. pentalene, the values of  $\lambda_p^{\max}$  are such that  $\lambda\delta < 1$  for values of  $\delta$  between zero and one, indicating convergence of the procedure. We shall return to a discussion of this matter later.

TABLE: 3.1

THE EIGENVALUES OF THE SUPERMATRIX,  $2 \underline{A} \underline{E} \underline{A}^{\dagger}$

Butadiene	Naphthalene	Pentalene
0.000	0.000	0.000
0.000	0.000	0.047
0.537	0.000	0.061
	0.017	0.103
	0.026	0.252
	0.146	0.426
	0.233	0.550
	0.273	0.552
	0.383	2.367
	0.721	
	1.034	

## CHAPTER 4

### A STUDY OF THE FINITE SYSTEMS

#### 4.10: INTRODUCTION

In the last chapter, we obtained the convergence criterion for the iterative procedure applicable to  $\pi$ -electron systems. According to the criterion, the eigenvalues of the supermatrix,  $\delta \underline{A} \underline{E} \underline{A}^\dagger$ , must be less than unity. In addition to determining the eigenvalues, one might examine the elements of the matrix  $\underline{A} \underline{E} \underline{A}^\dagger$  as they contribute to the  $n^{\text{th}}$  iterated bond order. Clearly, this is unlikely to be fruitful in the general case (because, in general, the many elements of  $\underline{A} \underline{E} \underline{A}^\dagger$  will be different). However, the matrix  $(\underline{A} \underline{E} \underline{A}^\dagger)$  is reduced in particular cases to a form amenable to analysis. For example, the linear polyenes, which, within the scheme explained in the section (3.20) of the last chapter, can be represented by continuant matrices, yield a much reduced form of  $\underline{A} \underline{E} \underline{A}^\dagger$ . This reduction of  $\underline{A} \underline{E} \underline{A}^\dagger$  for linear polyenes can be readily illustrated since the orthogonal matrices that diagonalize the hamiltonian are well-known. (For example, their usefulness is well documented in studies of lattice dynamics problems.<sup>34-36</sup>)

#### 4.20: AN EXTENSION OF THE PERTURBATION ANALYSIS TO CONTINUANT MATRICES

##### 4.201: The Eigenvalues and the Eigenvectors of the Continuant Matrices

As indicated in section 4.10, the matrix representation of the hamiltonian for linear polyenes can be written as a continuant

matrix<sup>†</sup>.

$$\underline{H} = \begin{bmatrix} H_{11} & H_{12} & & & \\ H_{21} & H_{22} & H_{23} & & \\ & & H_{32} & H_{33} & H_{34} \\ & & & & \\ & & & & \end{bmatrix} \quad (4-1)$$

H can be cast into a much simpler form, on assuming that all the core matrix elements,  $H_{\alpha\alpha}$ , are identical and the bond integrals the same. (In lattice dynamics problems, a similar assumption is that there is no impurity at each core element.) Thus,

$$^\dagger \quad H_{rs} = \chi_r |H_{\text{eff}}| \chi_s.$$

$N$  denotes the order of the matrix.

A continuant matrix model is valid for linear polyenes only if non-neighbour interactions are neglected and the A.O. overlap is omitted.



$$\underline{H} = \begin{bmatrix} H_{\alpha\alpha} & \beta & & & \\ \beta & H_{\alpha\alpha} & \beta & & \\ & \beta & H_{\alpha\alpha} & \beta & \\ & & \beta & H_{\alpha\alpha} & \beta \\ & & & \beta & H_{\alpha\alpha} \end{bmatrix} \quad (4-2)$$

The eigenvalues of  $\underline{H}$  are easily found to be

$${}^{(0)}E_j = H_{\alpha\alpha} + 2\beta \cos [j\pi/N + 1] \quad (4-3)$$

The orthogonal matrix which brings  $\underline{H}$  to the diagonal form has the elements

$${}^{(0)}C_{rj} = (2/N + 1)^{1/2} \sin (\pi rj/N + 1); \quad (4-4)$$

$$r, j = 1, 2, \dots N$$

#### 4.202: The Reduced $n^{\text{th}}$ Iterated Column Vector

For the continuant representation of linear polyenes, we shall only consider nearest neighbour bond orders and hence the dimension

T of the  $n^{\text{th}}$  iterated column vector  ${}_{(n)}\underline{\mathbf{P}}$  is reduced to  $(N - 1)$ . Further, this is consistent with a representation of  ${}_{(0)}\underline{\mathbf{H}}^{(1)}$  in which the only nonzero elements are those representing the nearest neighbour perturbations; i.e. the dimension of  ${}_{(0)}\underline{\mathbf{H}}^{(1)}$  can be reduced. Consequently in

$$\sum_Q (\underline{\mathbf{A}} \underline{\mathbf{E}} \underline{\mathbf{A}}^\dagger)_{TQ} {}_{(0)}\underline{\mathbf{H}}_Q^{(1)},$$

which occurs in  ${}_{(n)}\underline{\mathbf{P}}$  as given by equation (3-42),  $Q$  is reduced to a set of labels representing nearest neighbour pairs only and  $(\underline{\mathbf{A}} \underline{\mathbf{E}} \underline{\mathbf{A}}^\dagger)$  to a square matrix of order  $(N - 1)$ .

The  $n^{\text{th}}$  iterated super column vector, then, is

$$\left( {}_{(n)}\underline{\mathbf{P}} \right) \approx \left( {}_{(0)}\underline{\mathbf{P}} \right) + \left\{ \delta \underline{\mathbf{C}} (1 - \delta \underline{\mathbf{C}})^{-1} \right\} {}_{(0)}\underline{\mathbf{H}}^{(1)} \quad (4-5)$$

where  $\underline{\mathbf{C}} = \underline{\mathbf{A}} \underline{\mathbf{E}} \underline{\mathbf{A}}^\dagger$ .

#### 4.30: FORMAL SIMPLIFICATION OF THE SUPERMATRIX ELEMENTS, $\underline{\mathbf{A}} \underline{\mathbf{E}} \underline{\mathbf{A}}^\dagger$ .

In section 4.202, we obtained an expression for the  $n^{\text{th}}$  iterated density matrix as a super column vector with a reduced dimensionality. However, no simplification of the supermatrix elements has been effected. We consider this aspect in the following section:

#### 4.301: The Parity Relations

Examining the PQ element of the supermatrix  $\underline{\mathbf{C}}$ , it can be seen that since  $\underline{\mathbf{E}}$  is diagonal, this element results from a summation over I.

(The significance of the pair symbols<sup>s</sup> P,Q,..... I has been given in section (3.2032)). For the continuant matrix model this summation in the expanded form is

$$\begin{aligned} \sum_I (A_{PI} E_{I-IQ} A_I^\dagger) = & \sum_{i=1}^{N/2} \sum_{j=\frac{N}{2}+1}^N \left( \begin{pmatrix} (0)C_{ri}^{(0)} & (0)C_{r+1,j}^{(0)} \\ (0)C_{r+1,i}^{(0)} & (0)C_{rj}^{(0)} \end{pmatrix} E_{ij} \right. \\ & \left. \begin{pmatrix} (0)C_{si}^{(0)} & (0)C_{s+1,j}^{(0)} \\ (0)C_{s+1,i}^{(0)} & (0)C_{sj}^{(0)} \end{pmatrix} \right) \end{aligned} \quad (4-6)$$

Substituting the explicit form for the coefficients as given by equation (4-4) into equation (4-6) yields

$$\begin{aligned} & \sum_{i=1}^{N/2} \sum_{j=\frac{N}{2}+1}^N (\sin r\theta_i \sin(r+1)\theta_j + \sin(r+1)\theta_i \sin r\theta_j) \\ & E_{ij} (\sin s\theta_i \sin(s+1)\theta_j + \sin(s+1)\theta_i \sin s\theta_j) \end{aligned} \quad (4-7)$$

where  $\theta_i = (i\pi/N+1)$ ,  $\theta_j = (j\pi/N+1)$  and the normalization constants are absorbed in  $E_{ij}$  for convenience. It can be readily proved that

---

<sup>s</sup> The pairs P,Q ... are made up of neighbours only.

$$(\sin r\theta_i \sin(r+1)\theta_j + \sin(r+1)\theta_i \sin r\theta_j)$$

$$\neq 0 \text{ for } i, j \text{ odd (or even)}$$

$$= 0 \text{ for } i \text{ odd, } j \text{ even; or } i \text{ even, } j \text{ odd.} \quad (4-8)$$

The parity relations of equation (4-8) clearly reduce the number of terms that contribute to  $(\underline{A} \underline{E} \underline{A}^\dagger)_{PQ}$  in equation (4-6).

#### 4.302: The Influence of a Single Perturbation

In addition to the above simplification of the elements of the supermatrix,  $\underline{A} \underline{E} \underline{A}^\dagger$ , one might also consider contracting the  $n^{\text{th}}$  iterated super-column vector by an appropriate choice of the perturbation,  $(0)\widetilde{H}^{(1)}$ .

We consider linear polyenes where there are two types of bonds and impose a restriction that the initial perturbation,  $(0)\widetilde{H}^{(1)}$ , alternates along the chain, corresponding to the "single" and "double" bond character. Thus,  $(0)\widetilde{H}^{(1)}$  has the same magnitude on each bond but differs in sign from bond to bond. Clearly, imposing a definite form to  $(0)\widetilde{H}^{(1)}$  is a restriction on the iterative method as defined in chapter 2. However, in order to determine how a

---

<sup>†</sup> It should be borne in mind that in the parity relation, the values  $i$  and  $j$  can take are controlled by the inequalities:

$$N/2 \geq i \geq 1 \quad \text{and} \quad N \geq j \geq (N/2 + 1)$$

single perturbation, defined in the above sense, would influence the  $n^{\text{th}}$  iterated super-column vector given in equation (4-7), we first equate  ${}_{(0)}H^{(1)}$  to  ${}_{(0)}\Delta\tilde{P}^{(1)}$  and on adding the standard super-column vector  $-\{\tilde{P}\}_{\text{std}}$  to either side of the equation, we obtain:

$$\left\{ {}_{(n)}\Delta\tilde{P} \right\} \approx \left\{ {}_{(0)}\Delta\tilde{P}^{(1)} \right\} + \left\{ \delta\mathcal{C}(1 - \delta\mathcal{C})^{-1} \right\} \left( {}_{(0)}\Delta\tilde{P}^{(1)} \right) \quad (4-9)$$

where

$$\left( {}_{(n)}\Delta\tilde{P} \right) = \left( {}_{(n)}\tilde{P} \right) - \left( {}_{(0)}\tilde{P} \right)_{\text{std}} \quad \text{and}$$

$$\left( {}_{(0)}\Delta\tilde{P} \right) = \left( {}_{(0)}\tilde{P} \right) - \left( {}_{(0)}\tilde{P} \right)_{\text{std}}$$

Equation (4-9) immediately yields

$${}_{(n)}\Delta\tilde{P} \approx [(\underline{1} - \delta \underline{A} \underline{E} \underline{A}^\dagger)^{-1}] {}_{(0)}\Delta\tilde{P}^{(1)} \quad (4-10)$$

where  $\underline{1}$  is the unit matrix. Introducing the alternating perturbation into (4-10) gives

$${}_{(n)}\Delta\tilde{P} \approx {}_{(0)}\Delta\tilde{P}^{(1)} [\underline{\Omega}] (\underline{d}) \quad (4-11)$$

where  $\underline{\Omega} = (\underline{1} - \delta \underline{A} \underline{E} \underline{A}^\dagger)^{-1}$  and

$$\underline{d} = \begin{bmatrix} 1 \\ -1 \\ 1 \\ -1 \\ \vdots \end{bmatrix}$$

Clearly, the  $n^{\text{th}}$  iterated change,  $(n)\Delta P_T$  for a pair T is given by

$$(n)\Delta P_T \approx (0)\Delta P^{(1)} \left[ \sum_Q^{N-1} [\underline{\Omega}]_{TQ} (\underline{d})_Q \right] \quad (4-12)$$

We shall consider the implications of  $\underline{\Omega}$ , the inverse of the 'residual polarizability',<sup>†</sup>  $(\underline{1} - \delta \underline{C})$ , in the following section.

#### 4.40: THE ELUCIDATION OF $\underline{\Omega}$

Aside from the fact that the supermatrix  $\underline{C}$ , from which the 'residual polarizability' and its inverse are constructed is identical to its transpose, there exists an additional symmetry about the central bond which requires that:

$$\begin{aligned} & \sum_{i=1}^{N/2} \sum_{j=\frac{N}{2}+1}^N \left( (0)C_{ri}^{(0)} (0)C_{r+1,j}^{(0)} + (0)C_{r+1,i}^{(0)} (0)C_{rj}^{(0)} \right) \\ & E_{ij} \left( (0)C_{N-r+1,i}^{(0)} (0)C_{N-r,j}^{(0)} + (0)C_{N-r,i}^{(0)} (0)C_{N-r+1,j}^{(0)} \right) \\ & \equiv \sum_{i=1}^{N/2} \sum_{j=\frac{N}{2}+1}^N \left( (0)C_{N-r+1,i}^{(0)} (0)C_{N-r,j}^{(0)} + (0)C_{N-r,i}^{(0)} \right. \\ & \quad \left. (0)C_{N-r+1,j}^{(0)} \right) \end{aligned}$$

---

<sup>†</sup> The name 'residual polarizability matrix' is given to  $(\underline{1} - \delta \underline{A} \underline{E} \underline{A}^{\dagger})$  since the  $\delta$  times the polarizability matrix is removed from the unit matrix. No additional significance can be assigned at this time.

$$E_{ij} \left( \begin{pmatrix} (0)C_{ri}^{(0)} & (0)C_{r+1,j}^{(0)} \\ (0)C_{r+1,i}^{(0)} & (0)C_{rj}^{(0)} \end{pmatrix} \right) \quad (4-13a)$$

and

$$\begin{aligned} & \sum_{i=1}^{N/2} \sum_{j=\frac{N+1}{2}}^N \left( \begin{pmatrix} (0)C_{ri}^{(0)} & (0)C_{r+1,j}^{(0)} \\ (0)C_{r+1,i}^{(0)} & (0)C_{rj}^{(0)} \end{pmatrix} \right) E_{ij} \\ & \left( \begin{pmatrix} (0)C_{ri}^{(0)} & (0)C_{r+1,j}^{(0)} \\ (0)C_{r+1,i}^{(0)} & (0)C_{rj}^{(0)} \end{pmatrix} \right) \\ & \equiv \sum_{i=1}^{N/2} \sum_{j=\frac{N+1}{2}}^N \left( \begin{pmatrix} (0)C_{N-r,i}^{(0)} & (0)C_{N-r+1,j}^{(0)} \\ (0)C_{N-r+1,i}^{(0)} & (0)C_{N-r,j}^{(0)} \end{pmatrix} \right) E_{ij} \\ & \left( \begin{pmatrix} (0)C_{N-r,i}^{(0)} & (0)C_{N-r+1,j}^{(0)} \\ (0)C_{N-r+1,i}^{(0)} & (0)C_{N-r,j}^{(0)} \end{pmatrix} \right) \quad (4-13b) \end{aligned}$$

Thus, symmetry considerations indicate that certain rows (or columns) in  $\underline{C}$  are identical, making  $\underline{A} \underline{E} \underline{A}^\dagger$  singular. However, except for pathological cases (which will be referred to in Chap.

7) the residual matrix  $(\underline{1} - \delta \underline{A} \underline{E} \underline{A}^\dagger)$  will be taken to be non-singular. Hence, for both  $(\underline{1} - \delta \underline{A} \underline{E} \underline{A}^\dagger)$  and its inverse,  $(\underline{1} - \delta \underline{A} \underline{E} \underline{A}^\dagger)^{-1}$ , symmetry is conserved. Having considered the symmetry of  $\underline{\Omega}$ , we will now consider an illustrative example.

#### 4.401: An Illustrative Example

For butadiene, the inverse of the 'residual polarizability

matrix',  $(\underline{1} - \delta \underline{A} \underline{E} \underline{A}^\dagger)^{-1}$ , using the symmetry properties given in equations (4-13a) and (4-13b) and  $\pi_{12,12} = \pi_{34,34} = \pi_{12,34} = \pi_{34,12}$ , as given by equation (4-14) is given on page 45 as equation (4-17).

Knowing the inverse, (equation 4-17), the  $n^{\text{th}}$  iterated matrix elements for the (1-2) bond,  ${}_{(n)}\Delta P_1$ , and (2-3) bond,  ${}_{(n)}\Delta P_2$ , can be obtained as in equations (4-15) and (4-16).

$$\delta \underline{A} \underline{E} \underline{A}^\dagger = 2\underline{\pi} \quad (4-14)$$

$$\begin{aligned} {}_{(n)}\Delta P_1 &= {}_{(0)}\Delta P_1^{(1)} \sum_Q^3 (-1)^{Q+1} (\underline{\Omega})_{1Q} \\ &= {}_{(0)}\Delta P_1^{(1)} 2[1 - \delta\pi_{23,23} - \delta\pi_{12,23}] / ||(\underline{1} - \delta\underline{\pi})|| \quad (4-15) \end{aligned}$$

and

$${}_{(n)}\Delta P_2 = {}_{(0)}\Delta P_2^{(1)} 2[-(1 - 2\delta\pi_{12,12} - 2\delta\pi_{12,23})] / ||(\underline{1} - \delta\underline{\pi})|| \quad (4-16)$$

In (4-12), it should be noted that due to symmetry in  ${}_{(0)}\tilde{H}^{(1)}$  ( or in  $\underline{d}$ ), the contribution  $(\delta^2\pi_{12,23}^2 + \delta\pi_{12,34}(1 - \pi_{23,23})) \underline{\Omega}_{11}$  is cancelled by the same term of  $\underline{\Omega}_{13}$ . Recognizing this, we can give a form for the "reduced" inverse of the residual polarizability matrix as



$$\underline{\Omega} = \frac{1}{||(\underline{1} - \delta \underline{\pi})||} \times$$

$$\begin{bmatrix} [(1 - \delta\pi_{23,23})(1 - \delta\pi_{12,12}) - \delta^2\pi^2_{12,23}] & [\delta\pi_{12,23}] & [\delta^2\pi^2_{12,23} + \delta\pi_{12,12}(1 - \delta\pi_{23,23})] \\ [\delta\pi_{23,12}] & [(1 - \delta\pi_{12,12})(1 - \delta\pi_{12,12}) - \delta^2\pi^2_{12,12}] & [\delta\pi_{23,34}] \\ [\delta^2\pi^2_{12,23} + (1 - \delta\pi_{23,23})\delta\pi_{12,12}] & [\delta\pi_{34,23}] & [(1 - \delta\pi_{12,12})(1 - \delta\pi_{23,23}) - \delta^2\pi^2_{12,23}] \end{bmatrix}$$

(4-17)

$$\underline{\Omega}_{\text{reduced}} = \frac{1}{||(\underline{1} - \delta\pi)||} \times$$

$$\begin{bmatrix} (1 - \delta\pi_{23,23}) & \delta\pi_{12,23} & 0 \\ \delta\pi_{23,12} & (1 - 2\delta\pi_{12,12}) & \delta\pi_{23,34} \\ 0 & \delta\pi_{34,23} & (1 - \delta\pi_{23,23}) \end{bmatrix}$$

(4-18)<sup>†</sup>

$$= \frac{1}{||(\underline{1} - \delta\pi)||} \begin{bmatrix} 1 - \delta\pi_{\ell\ell} & -\delta\pi_{\ell s} & 0 \\ -\delta\pi_{\ell s} & 1 - \delta\pi_{ss} & -\delta\pi_{\ell s} \\ 0 & -\delta\pi_{\ell s} & 1 - \delta_{\ell\ell} \end{bmatrix}$$

where  $\pi_{\ell\ell} = \pi_{23,23}$  = self polarizability of the central or long bond

$\pi_{ss} = \pi_{12,12} = \pi_{34,34}$  = self polarizability of the terminal or short bonds

$\pi_{\ell s} = \pi_{12,23} = \pi_{23,34}$  = mutual polarizability of the long bond by the neighbouring short bond.

---

<sup>†</sup> Equation (4-18) does not mean that  $\underline{\Omega}_{\text{reduced}} \equiv \underline{\Omega}$  even under symmetry restrictions. However,  $\underline{\Omega}_{\text{reduced}} (0)_{\underline{H}} \equiv \underline{\Omega} (0)_{\underline{H}}$ .

Equation (4-18) suggests that the  $n^{\text{th}}$  iterated matrix element for any bond in linear polyenes has its contributions coming from the self-polarizability of the neighbouring bond(s) and the mutual polarizability of the neighbouring bond with itself.

In Tables 4-1 - 4.4, we have given the values of the  $n^{\text{th}}$  iterated matrix elements for butadiene using the "Jacobi" diagonalization method and the closed-form expressions, (4-12), (4-15), (4-16) and (4-17). In both instances, a  $P(\text{standard})$  value which causes 'equal-but-opposite-in-sign' perturbations along the bonds and a  $P(\text{standard})$  value of unity were used. Clearly, the results of the calculations indicate that for low values of  $\delta$  the closed (but approximate) form of the  $n^{\text{th}}$  iterative bond order is very close to the self-consistent result using the Jacobi diagonalization.

TABLE: 4.1

THE  $n^{\text{th}}$  ITERATED BOND ORDER MATRIX ELEMENTS,  $(n)\Delta P$ , FOR  
BUTADIENE USING THE "JACOBI" METHOD

$\delta$	$P_{\text{std}}$	$(0)\Delta P_1 =$ $-(0)\Delta P_2$	$(1)\Delta P_1$	$(n)\Delta P_1$	$-(1)\Delta P_2$	$-(n)\Delta P_2$
0.2	0.6708	0.2236	0.2387	0.2403	0.2550	0.2586
0.6	0.6708	0.2236	0.2635	0.2763	0.3142	0.3499
1.2	0.6708	0.2236	0.2900	0.3217	0.3937	0.5484
2.0	0.6708	0.2236	0.3114	0.2936	0.4832	0.9351

TABLE: 4.2

THE  $n^{\text{th}}$  ITERATED BOND ORDER MATRIX ELEMENTS,  $(n)\Delta P$ , FOR  
BUTADIENE USING THE CLOSED-FORM APPROXIMATION

$\delta$	$P_{\text{std}}$	$(0)\Delta P_1 =$ $-(0)\Delta P_2$	$(1)\Delta P_1$	$(n)\Delta P_1$	$-(1)\Delta P_2$	$-(n)\Delta P_2$
0.2	0.6708	0.2236	0.2396	0.2415	0.2556	0.2594
0.6	0.6708	0.2236	0.2716	0.2944	0.3197	0.3685
1.2	0.6708	0.2236	0.3197	0.4932	0.4157	0.7628
2.0	0.6708	0.2236	0.3837	-1.9591	0.5438	-4.1418

TABLE: 4.3

THE  $n^{\text{th}}$  ITERATED BOND ORDER MATRIX ELEMENTS,  $(n)^{\Delta P}$ , FOR  
BUTADIENE USING THE "JACOBI" METHOD

$\delta$	$P_{\text{std}}$	$(0)^{\Delta P_1}$	$(0)^{\Delta P_2}$	$(1)^{\Delta P_1}$	$(n)^{\Delta P_1}$	$(1)^{\Delta P_2}$	$(n)^{\Delta P_2}$
0.2	1.0000	-0.1056	-0.5528	-0.0896	-0.0877	-0.5864	-0.5905
0.6	1.0000	-0.1056	-0.5528	-0.0581	-0.0397	-0.6640	-0.7209
1.2	1.0000	-0.1056	-0.5528	-0.0181	-0.0328	-0.8107	-1.2542
2.0	1.0000	-0.1056	-0.5528	-0.0028	-1.9692	-1.0668	-1.2461

TABLE: 4.4

THE  $n^{\text{th}}$  ITERATED BOND ORDER MATRIX ELEMENTS,  $(n)^{\Delta P}$ , FOR  
BUTADIENE USING THE CLOSED-FORM APPROXIMATION

$\delta$	$P_{\text{std}}$	$(0)^{\Delta P_1}$	$(0)^{\Delta P_2}$	$(1)^{\Delta P_1}$	$(n)^{\Delta P_1}$	$(1)^{\Delta P_2}$	$(n)^{\Delta P_2}$
0.2	1.0000	-0.1056	-0.5528	-0.0896	-0.0877	-0.5848	-0.5886
0.6	1.0000	-0.1056	-0.5528	-0.0576	-0.0347	-0.6489	-0.3932
1.2	1.0000	-0.1056	-0.5528	0.0095	+0.1642	-0.7449	0.0553
2.0	1.0000	-0.1056	-0.5528	0.0545	-2.2907	-0.8730	-5.4733

## CHAPTER 5

### A STUDY OF INFINITE SYSTEMS

#### 5.10: INTRODUCTION

The analysis of the iterative method given in the last two chapters was effectively limited to finite systems, for both determination of the eigenvalues of an infinite dimensional polarizability matrix and the investigation of an infinite number of contributions of  $(\underline{1} - \delta \underline{A} \underline{E} \underline{A}^\dagger)^{-1}$  to  $(n)^P$  are unrewarding. However, an analysis similar in spirit but differing in mathematical technique can be carried out readily for infinite cyclic systems. To illustrate the implications of the analysis, some numerical results will also be given.

#### 5.20: ANALYTICAL EXPRESSIONS FOR THE BOND ORDERS OF INFINITE CYCLIC POLYENES

A cyclic polyene with the general formula,  $C_{4n+2}H_{4n+2}$ , where  $n$  is large is considered for the present study. The results obtained here are equally valid for infinite linear chains.<sup>37</sup> The circular model is chosen simply for mathematical convenience.

Taking the carbon-carbon bonds to be alternately long ( $R_\ell$ ) and short ( $R_s$ ) such that the bond integral  $|H_\ell| \langle H_s \rangle^\dagger$  and following

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$$^\dagger H_\ell = \langle \chi_{2r-1} | \hat{H}_{\text{eff}} | \chi_{2r} \rangle_{\text{long}} \text{ and } H_s = \langle \chi_{2r} | \hat{H}_{\text{eff}} | \chi_{2r+1} \rangle_{\text{short}}$$

$\chi_{2r}$ 's are the A.O. basis and  $\hat{H}_{\text{eff}}$  is the one-particle effective hamiltonian.

Salem,<sup>38</sup> the normalised atomic orbital coefficients,  $C_{2r,j}$  and  $C_{2r+1,j}$ , for two adjacent centers  $2r$  and  $2r + 1$  separated by a double bond are found to be

$$C_{j,2r} = (4n + 2)^{-1/2} \left( H_L e^{-1/2 i \theta_j} + H_S e^{1/2 i \theta_j} / E \right)^{1/2} e^{1/2 i 2r \theta_j} \quad (5-1)$$

$$C_{j,2r+1} = (4n + 2)^{-1/2} \left( H_L e^{1/2 i \theta_j} + H_S e^{-1/2 i \theta_j} / E \right)^{1/2} \times e^{1/2 i (2r+1) \theta_j} \quad (5-2)$$

where

$$E_j = \left( H_L^2 + H_S^2 + 2H_L H_S \cos \theta_j \right)^{1/2} \quad (5-3)$$

and

$$\theta_j = \left( j\pi / (2n + 1) \right)$$

For the iterative analysis, expressions for the bond orders of the long and the short bonds are essential. From equations (5-1) and (5-2), the bond orders can be written as:

$$(0)^P_S = \sum_j^{\text{occupied}} \left( \eta C_{2r,j} C_{2r+1,j} \right)_{\text{short}}$$

$$= \left( 1 / (2n + 1) \right) \sum_{j=-n}^n \left( 1 + (0)^k \cos \theta_j \right) /$$

$$\left(1 + 2 (0)^k \cos \theta_j + (0)^{k^2}\right)^{\frac{1}{2}} \quad (5-4)$$

$$(0)^{P_\ell} = \left(1/2n + 1\right) \sum_{j=-n}^n \left((0)^k + \cos \theta_j\right) /$$

$$\left(1 + 2 (0)^k \cos \theta_j + (0)^{k^2}\right)^{\frac{1}{2}} \quad (5-5)$$

where  $k = (H_\ell/H_S)$  is the "bond alternation parameter" and  $n$  is the occupation number. The summation in equations (5-4) and (5-5) can be represented analytically for  $n \rightarrow \infty$  and yields:

$$(0)^{P_S} = \left[ \frac{1 + (0)^k}{\pi} \right] \mathbf{E} \left( \frac{2\sqrt{(0)^k}}{1 + (0)^k} \right) + \left[ \frac{1 - (0)^k}{\pi} \right] \mathbf{K} \left( \frac{2\sqrt{(0)^k}}{1 + (0)^k} \right) \quad (5-6)$$

and

$$(0)^{P_\ell} = \left[ \frac{1 + (0)^k}{(0)^k \pi} \right] \mathbf{E} \left( \frac{2\sqrt{(0)^k}}{1 + (0)^k} \right) - \left[ \frac{1 - (0)^k}{(0)^k \pi} \right] \mathbf{K} \left( \frac{2\sqrt{(0)^k}}{1 + (0)^k} \right) \quad (5-7)$$



Here  $\mathbf{K}\left(\frac{2\sqrt{(0)^k}}{1 + (0)^k}\right)$  and  $\mathbf{E}\left(\frac{2\sqrt{(0)^k}}{1 + (0)^k}\right)$  are the complete elliptic

integrals of the first and the second kind respectively. The modulus for which the elliptic integral is evaluated is given in parenthesis. It is quite useful if  $\mathbf{K}$  and  $\mathbf{E}$  for modulus

$$\left(2\sqrt{(0)^k}/1 + (0)^k\right)$$

can be expressed in terms of  $\mathbf{K}$  and  $\mathbf{E}$  for modulus  $(0)^k$ . Using the identity<sup>†</sup>

$$\mathbf{K}\left(\sqrt{(0)^k}/1 + (0)^k\right) = \left[1 + (0)^k\right] \mathbf{K}\left((0)^k\right) \quad (5-8)$$

and

$$\begin{aligned} \mathbf{E}\left(\sqrt{(0)^k}/1 + (0)^k\right) &= \left[\frac{1}{1 + (0)^k}\right] \\ &\quad \left[2\mathbf{E}\left((0)^k\right) - \left[1 - (0)^{k^2}\right]\mathbf{K}\left((0)^k\right)\right] \end{aligned} \quad (5-9)$$

where

---

<sup>†</sup> A description of these transformations is given in "Anwendung der Elliptischen Funktionen in Physik und Technik" by F. Oberhettinger und W. Magnus (Springer-Verlag, Berlin 1949).

$$\mathbf{K} \left( (0)^k \right) = \int_0^{\pi/2} (1 - (0)^{k^2} \sin^2 \phi)^{-\frac{1}{2}} d\phi \quad \text{and}$$

$$\mathbf{E} \left( (0)^k \right) = \int_0^{\pi/2} (1 - (0)^{k^2} \sin^2 \phi)^{\frac{1}{2}} d\phi$$

in equations (5-6) and (5-7), it can be shown that

$$(0)^p_s \left( \frac{2 \sqrt{(0)^k}}{1 + (0)^k} \right) = \frac{2}{\pi} \mathbf{E} \left( (0)^k \right) \quad (5-10)$$

and

$$(0)^p_\ell \left( \frac{2 \sqrt{(0)^k}}{1 + (0)^k} \right) = \frac{2}{\pi} \left( (0)^k \mathbf{K} \left( (0)^k \right) - \frac{\mathbf{K}}{(0)^k} + \frac{\mathbf{E}}{(0)^k} \right) \quad (5-11)$$

One other quantity that will be used in the functional analysis is the bond-order difference between the long and the short bonds which we write as:

$$\left\{ (0)^p_s \left( \frac{2 \sqrt{(0)^k}}{1 + (0)^k} \right) - (0)^p_\ell \left( \frac{2 \sqrt{(0)^k}}{1 + (0)^k} \right) \right\}$$

$$= \frac{2}{\pi} \left[ \left( \frac{1}{(0)^k} \right) \left( \mathbf{K} \left( (0)^k \right) - \mathbf{E} \left( (0)^k \right) \right) + \right.$$

$$\left. \left( \mathbf{E} \left( (0)^k \right) - (0)^k \mathbf{K} \left( (0)^k \right) \right) \right] \quad (5-12)$$

It is quite apparent that knowing the value for the bond alternation parameter,  $(0)^k$ , one would be able to obtain any of  $(0)^{P_s}$ ,  $(0)^{P_\ell}$  or the difference  $((0)^{P_s} - (0)^{P_\ell})$ .

### 5.30: THE $n^{\text{th}}$ ITERATED BOND ORDER TERMS

#### 5.301: The Iterative Scheme

As is evident from the section 6.10, the bond orders for the long and the short bonds are defined in terms of the complete elliptic integrals of the first kind and the second kind for a bond alternation parameter. With a knowledge of  $(0)^{P_d}$  and  $(0)^{P_s}$ , a new bond alternation parameter  $(1)^k$  can be obtained using either Salem's relation (equation 2-3) to give:<sup>†</sup>

$$(1)^k = \left( (1)^{H_\ell} / (1)^{H_s} \right) = (0)^k \exp \left( -\xi \left( (0)^{P_\ell} - (0)^{P_s} \right) \right) \quad (5-13)^{\S}$$

or the relation given by equation (2-6) to give

$$(1)^k = (1)^{H_\ell} / (1)^{H_s} = \left[ (0)^{H_\ell} + \delta \left( (0)^{P_\ell} - P_{\text{std}} \right) \right] / \left[ (0)^{H_s} + \delta \left( (0)^{P_s} - P_{\text{std}} \right) \right] \quad (5-14)$$

$P_{\text{std}}$  is the bond order of a standard bond.

<sup>†</sup> Equation (5-13) is obtained by substituting the Coulson-

Golebiewski relation  $R = 1.517 - 0.18 P$  into Salem's equation

$(1)^H = (0)^{H^{(0)}} \exp \left( - (R - R_{\text{std}}) / 0.3106 \right)$  and then using the resulting equation to define  $(1)^{H_\ell}$  and  $(1)^{H_s}$  in  $(1)^k$ .

<sup>§</sup>  $\xi = 0.18 / 0.3106$ .

The new alternation parameter would then allow one to find the quantities  $P_s$  and  $P_\ell$  and this process, on repetition would form the basis for the iterative analysis. In the last two chapters, the iterative procedure was followed by examining the  $n^{\text{th}}$  iterated term for the bond order of a bond or the bond order matrix cast into a column vector. In the present analysis, since the bond alternation parameter at each stage of the iteration is related to the bond orders of the long and the short bond of the previous iteration, we follow the iterative procedure by asking for the difference between two bond order quantities, i.e.  $P_s - P_\ell$ , on using Salem's relation, or  $P_\ell = (0)^k P_s$  on using equation (5-14).

#### 5.302: The Use of Salem's Relation

Using Salem's relation (equation 5-13), a general form for the bond alternation parameter at the  $n^{\text{th}}$  stage of the iteration can be given as

$$(n)^k = (0)^k \exp \left( -\xi \left( (n-1)^{P_\ell} - (n-1)^{P_s} \right) \right) \quad (5-15)$$

For a small value of the initial bond alternation parameter  $(0)^k$  we can expand the elliptic integrals in equations (5-10) and (5-11) to give;

$$(0)^{P_\ell} \simeq (0)^{k/2} \quad (5-16a)$$

and

$$({}_0)P_s \simeq 1 - \left( ({}_0)k/2 \right)^2 \quad (5-16b)$$

Based on equations (5-16a) and (5-16b), a new bond alternation parameter  $({}_1)k$  is evaluated using (5-15). A cyclic repetition of (5-16a), (5-16b) and (5-15) gives, explicitly, the basis of the iterative procedure. It is assumed that the bond alternation parameter,  $k$ , remains small at all stages of the iterative procedure. To a first order approximation, from (5-15), (5-16a) and (5-16b), one can immediately write that

$$\begin{aligned} \left( ({}_1)P_s - ({}_1)P_\ell \right) &\approx \left( ({}_0)P_s - ({}_0)P_\ell \right) + \xi \left( ({}_0)P_s - ({}_0)P_\ell \right) \times \\ &\quad \left( \frac{1}{2} \left( ({}_0)k + ({}_0)k^2 \right) \right) \end{aligned} \quad (5-17)$$

where  $\xi$  has been defined earlier. Continuing this further, it can be shown that

$$\begin{aligned} \left( ({}_2)P_s - ({}_2)P_\ell \right) &\approx \left( ({}_0)P_s - ({}_0)P_\ell \right) + \xi \left( ({}_0)P_s - ({}_0)P_\ell \right) \times \\ &\quad \left( \frac{1}{2} \left( ({}_1)k + ({}_1)k^2 \right) \right) \end{aligned}$$

$$\begin{aligned}
 &\simeq \left( (0)^{P_S} - (0)^{P_\ell} \right) + \xi \left( (0)^{P_S} - (0)^{P_\ell} \right) \\
 &\quad \left( \frac{1}{2} \left( (0)^k + (0)^{k^2} \right) \right) + \xi^2 \left( (0)^{P_S} - (0)^{P_\ell} \right) \\
 &\quad \left( \frac{1}{2} \left( (0)^k + (0)^{k^2} \right) \right) \left( \frac{1}{2} \left( (0)^k + (0)^{k^2} \right) \right) \quad (5-18)
 \end{aligned}$$

Following this, the  $n^{\text{th}}$  iterated difference,  $\left( (n)^{P_S} - (n)^{P_\ell} \right)$ , is written as

$$\begin{aligned}
 \left( (n)^{P_S} - (n)^{P_\ell} \right) &\simeq \left( (0)^{P_S} - (0)^{P_\ell} \right) + \\
 &\quad \left\{ \sum_{n=1}^n \left( \xi \left( \frac{1}{2} \left( (0)^k + (0)^{k^2} \right) \right) \right)^n \right\} \\
 &\quad \left\{ (0)^{P_S} - (0)^{P_\ell} \right\} \quad (5-19)
 \end{aligned}$$

Since  $\xi \left( \frac{1}{2} \left( (0)^k + (0)^{k^2} \right) \right)$  is always less than unity, for  $n \rightarrow \infty$ , equation (5-19) is immediately written as

$$\left( (n)^{P_S} - (n)^{P_\ell} \right) \simeq \left( (0)^{P_S} - (0)^{P_\ell} \right) / \left( 1 - \xi \left( \frac{1}{2} \left( (0)^k + (0)^{k^2} \right) \right) \right) \quad (5-20)$$

In section 5.40, the values of  $(n)^{P_S} - (n)^{P_\ell}$  obtained using the approximate form (equation 5.20) are indicated and compared with results for  $\left( (n)^{P_S} - (n)^{P_\ell} \right)$  obtained by carrying out the full iterated procedure to convergence.

### 5.303: The Use of a Linear Relation

Clearly, there appears to be no serious difficulty in following the iterative method which uses Salem's relation for the perturbation. The procedure is not so clear cut on using our form of the perturbation in the iterative method.

The equation for the  $n^{\text{th}}$  iterated bond alternation parameter is given by

$$\begin{aligned} (n)^k = & \left[ (0)^{H_L} + \delta \left( P_{\text{std}} - (n-1)^{P_L} \right) \right] \cdot \\ & \left[ (0)^{H_S} + \delta \left( P_{\text{std}} - (n-1)^{P_S} \right) \right]^{-1} \quad (5-21)^{\dagger} \end{aligned}$$

Without any approximation, if successive substitutions are made at each stage of the iteration, we would come up with continued fractions in the numerator and in the denominator, which are found to be difficult to resolve. Hence, approximations are made starting with  $(1)^k$ .

$$(1)^k = \left[ (0)^{H_L} + \delta \left( P_{\text{std}} - (0)^{P_L} \right) \right] \left[ (0)^{H_S} + \delta \left( P_{\text{std}} - (0)^{P_S} \right) \right]^{-1}$$

---

<sup>†</sup> A positive value of  $\delta$  here corresponds to using a negative value in our relation (2-6) for  $(1)^{H_L}$  and  $(1)^{H_S}$ .

Dividing the numerator and the denominator of the above equation by  ${}_{(0)}H_s$ , considering low values of  ${}_{(0)}k$  and requiring that

$$\left| \frac{\delta}{{}_{(0)}H_s} (P_{std} - {}_{(0)}P_s) \right|^2 \ll 1 ,$$

one obtains

$$\begin{aligned} {}_{(1)}k &\approx {}_{(0)}k + \delta' (P_{std} - {}_{(0)}k P_{std}) \\ &\quad - \delta' ({}_{(0)}P_\ell - {}_{(0)}k {}_{(0)}P_s) \\ &\quad - \delta'^2 (P_{std} - {}_{(0)}P_\ell) (P_{std} - {}_{(0)}P_s) \end{aligned} \quad (5-22)$$

where  $\delta' = (\delta / {}_{(0)}H_s)$ . Again, for a low value of  ${}_{(0)}k$ , the last term can be neglected. Defining

$$\delta' ({}_{(0)}P_\ell - {}_{(0)}k {}_{(0)}P_s) = {}_{(0)}\delta' \quad \text{and}$$

$$\delta' (P_{std} - {}_{(0)}k P_{std}) = \delta''$$

and recognizing that the density matrix elements which are expressed in terms of the complete elliptic integrals of the first and the second kind can be simplified for a low value of the alternation parameter, the expression for



$$\left( (1)P_{\ell} - (0)^k (1)P_s \right)$$

is obtained as

$$\begin{aligned} \left( (1)P_{\ell} - (0)^k (1)P_s \right) &\approx \left( (1)\frac{k}{2} - (0)^k + (0)^k \left( (1)\frac{k}{2} \right)^2 \right) \\ &\approx \left\{ \left( (0)\frac{k}{2} + (0)\frac{\delta''}{2} - (0)\frac{\delta'}{2} \right) \right. \\ &\quad \left. - (0)^k + (0)\frac{k}{4} \left( (0)^k + \delta'' - (0)\delta' \right)^2 \right\} \end{aligned} \quad (5-23)$$

Within the approximations made earlier in this section,

$$\begin{aligned} \left( (1)P_{\ell} - (0)^k (1)P_s \right) &\approx \left( (0)P_{\ell} - (0)^k (0)P_s \right) \\ &\quad + \delta'' \left( \frac{1}{2} \left( 1 + (0)k^2 \right) \right) \\ &\quad - (0)\delta' \left( \frac{1}{2} \left( 1 + (0)k^2 \right) \right) \end{aligned} \quad (5-24)$$

The second term on the right hand side of equation (5-24) does not change from iteration to iteration.

The new bond alternation parameter is then obtained from

$$({}_2)^k \approx ({}_0)^k + \delta'' - ({}_1)^{\delta'} \quad (5-25)$$

For this bond-alternation parameter, the equation for

$$\left( ({}_2)^{P_\ell} - ({}_0)^k ({}_2)^{P_s} \right)$$

is:

$$\begin{aligned} \left( ({}_2)^{P_\ell} - ({}_0)^k ({}_2)^{P_s} \right) &\approx \left( ({}_0)^{P_\ell} - ({}_0)^k ({}_0)^{P_s} \right) \\ &+ \delta'' \left( \frac{1}{2} (1 + ({}_0)^{k^2}) \right) \left( 1 - \frac{\delta'}{2} (1 + ({}_0)^{k^2}) \right) \\ &- ({}_0)^{\delta'} \left( \frac{1}{2} (1 + ({}_0)^{k^2}) \right) \left( 1 - \frac{\delta'}{2} (1 + ({}_0)^{k^2}) \right) \end{aligned} \quad (5-26)$$

Repeating this procedure, the  $n^{\text{th}}$  iterated difference yields

$$\begin{aligned} \left( ({}_n)^{P_\ell} - ({}_0)^k ({}_n)^{P_s} \right) &\approx \left( ({}_0)^{P_\ell} - ({}_0)^k ({}_0)^{P_s} \right) \\ &+ \delta' \left( \frac{1}{2} (1 + ({}_0)^{k^2}) \right) \left\{ \sum_{n=1} (-1)^{n-1} \left( \frac{\delta'}{2} (1 + ({}_0)^{k^2}) \right)^{n-1} \right\} \times \\ &\left( ({}_0)^{P_{\text{std}}} - ({}_0)^k P_{\text{std}} \right) \end{aligned}$$

$$- \delta' \left( \frac{1}{2} \left( 1 + {}_{(0)}k^2 \right) \right) \left\{ \sum_{n=1} (-1)^{n-1} \left( \frac{\delta}{2} \left( 1 + {}_{(0)}k^2 \right) \right)^{n-1} \right\} \\ \left( {}_{(0)}P_{\ell} - {}_{(0)}k {}_{(0)}P_s \right) \quad (5-27)$$

(The substitution for  $\delta''$  and  ${}_{(0)}\delta'$  is made in getting (5-27).)

For  $\delta' \left( \frac{1}{2} \left( 1 + {}_{(0)}k^2 \right) \right) < 1$  and  $n \rightarrow \infty$ , equation (5-27)

yields

$$\left( {}_{(n)}P_{\ell} - {}_{(0)}k {}_{(n)}P_s \right) \approx \left( {}_{(0)}P_{\ell} - {}_{(0)}k {}_{(0)}P_s \right) \\ + \delta' \left( \frac{1}{2} \left( 1 + {}_{(0)}k^2 \right) \right) \left( P_{std} - {}_{(0)}k P_{std} \right) \\ / \left( 1 - \delta' \left( \frac{1}{2} \left( 1 + {}_{(0)}k^2 \right) \right) \right) - \\ \delta' \left( \frac{1}{2} \left( 1 + {}_{(0)}k^2 \right) \right) \left( {}_{(0)}P_{\ell} - {}_{(0)}k {}_{(0)}P_s \right) \\ / \left( 1 - \delta' \left( \frac{1}{2} \left( 1 + {}_{(0)}k^2 \right) \right) \right) \quad (5-28)$$

The validity of the approximation leading to (5-28) is checked by comparing results obtained by the iterative method.

The details are given in the following section.

### 5.304: Numerical Investigations

#### 5.3041: Assessment of Approximations

Although closed form expressions were obtained for  $(n)^P$  using both Salem's relation and our linear relation, a number of approximations were required. In both instances higher order terms were dropped since a small value of  $(0)^k$  was invoked. These approximations can be readily investigated for particular cases. In addition, a truncated binomial expansion was employed when our linear relation was used for the iterative procedure. To assess the validity of these approximations, numerical calculations were carried out using both the closed form expressions and the standard expressions carried from iteration to iteration. (Note that negative values only were assigned to the perturbation parameter,  $\delta$ , since a positive value can preclude the evaluation of the elliptic integral of the first kind, **K**.) The results are given in Tables 5.1 and 5.2. It would appear that for small values of  $(0)^k$  (see figures 1 - 4) we could forego the iterative process and use the closed form expression directly.

#### 5.3042: Convergence

In the calculations using our relations it was noticed that oscillations in the bond order elements from iteration to iteration occurred. From the closed form expressions given by equation (5-27), it is clear that this is a result of a negative value for the ratio in the geometric series. Clearly equation

(5-27) is a geometric series and converges only if  $\delta' \frac{1}{2}(1 + {}_{(0)}k^2)$  is less than unity in magnitude. That the oscillations and convergence rate are dependent on the value of  $\delta$  can be seen by considering the curves displayed in figures 1 - 4.

TABLE: 5.1

THE RESULTS FOR  $\left( (n)P_s - (n)P_\ell \right)$  USING THE  
"EXACT" EQUATIONS AND THE CLOSED FORM EXPRESSION

E	$(0)^k$	$\left( (0)P_s - (0)P_\ell \right)$	$\frac{\left( (0)P_s - (0)P_\ell \right)}{\left( 1 - E\left( \frac{1}{2} \left( (0)^k + (0)^{k^2} \right) \right) \right)}^\dagger$	$\left( (n)P_s - (n)P_\ell \right)^\S$
0.5795	0.10101	0.94687	0.97840	0.97038
0.5795	0.25000	0.85819	0.94363	0.92112
0.5795	0.40404	0.75142	0.89922	0.86120
0.5795	0.66667	0.52140	0.76896	0.72565
0.5795	0.85714	0.29020	0.53864	0.57270

<sup>§</sup> By the exact calculation, (use of equation (5-12)).

<sup>†</sup> By the closed form expression, (use of equation (5-28)).

TABLE: 5.2

THE RESULTS FOR  $\left( (n)^P_\ell - (0)^k (n)^P_s \right)$  USING  
THE "EXACT" EQUATIONS AND THE CLOSED FORM EXPRESSION\*

$(0)^k$	$\delta'$	$(0)^P_\ell - (0)^k (0)^P_s$	$(n)^P_\ell - (0)^k (n)^P_s$	
			Numerical <sup>†</sup> (Elliptic Integrals)	Analytical <sup>§</sup>
0.20202	0.2020	-0.09841	-0.00991	-0.01628
0.20202	0.4040	-0.09841	0.06443	0.08788
0.20202	0.6061	-0.09841	0.12535	0.22373
0.20202	0.8081	-0.09841	0.17059	0.40921
0.20202	1.0101	-0.09841	0.11033	0.67697
0.20202	1.2121	-0.09841	0.06452	1.09685
0.55556	0.2222	-0.2198	-0.12185	-0.18158
0.55556	0.4444	-0.2198	-0.04792	-0.12769
0.55556	0.6666	-0.2198	-0.00280	-0.04600
0.55556	0.8888	-0.2198	-0.22501	0.09233
0.55556	1.1111	-0.2198	-0.30080	0.37842
0.55556	1.3333	-0.2198	-0.34409	1.31606

<sup>†</sup> By the "exact" calculation. (Equations 5-10 and 5-11).

<sup>§</sup> By the closed form expression, 5-28.

\* n large and even is considered.

TABLE: 5.2 cont'd

THE RESULTS FOR  $\left( (n)^P_\ell - (0)^k (n)^P_s \right)$  USING THE  
"EXACT" EQUATIONS AND THE CLOSED FORM EXPRESSION\*

$(0)^k$	$\delta'$	$(0)^P_\ell - (0)^k (0)^P_s$	$(n)^P_\ell - (0)^k (n)^P_s$	
			Numerical <sup>†</sup> (Elliptic Integrals)	Analytical <sup>§</sup>
0.77778	0.2222	-0.2132	-0.12504	-0.21124
0.77778	0.4444	-0.2132	-0.06851	-0.12316
0.77778	0.6666	-0.2132	-0.22972	0.20280
0.77778	0.8888	-0.2132	-0.35608	0.19070
0.77778	1.1111	-0.2132	-0.43140	0.13890
0.77778	1.3333	-0.2132	-0.48545	0.07532

<sup>†</sup> By the "exact" calculation, (equations (5-10) and (5-11)).

<sup>§</sup> By the closed form expression, (equation (5-28)).

\* n large and even is considered.



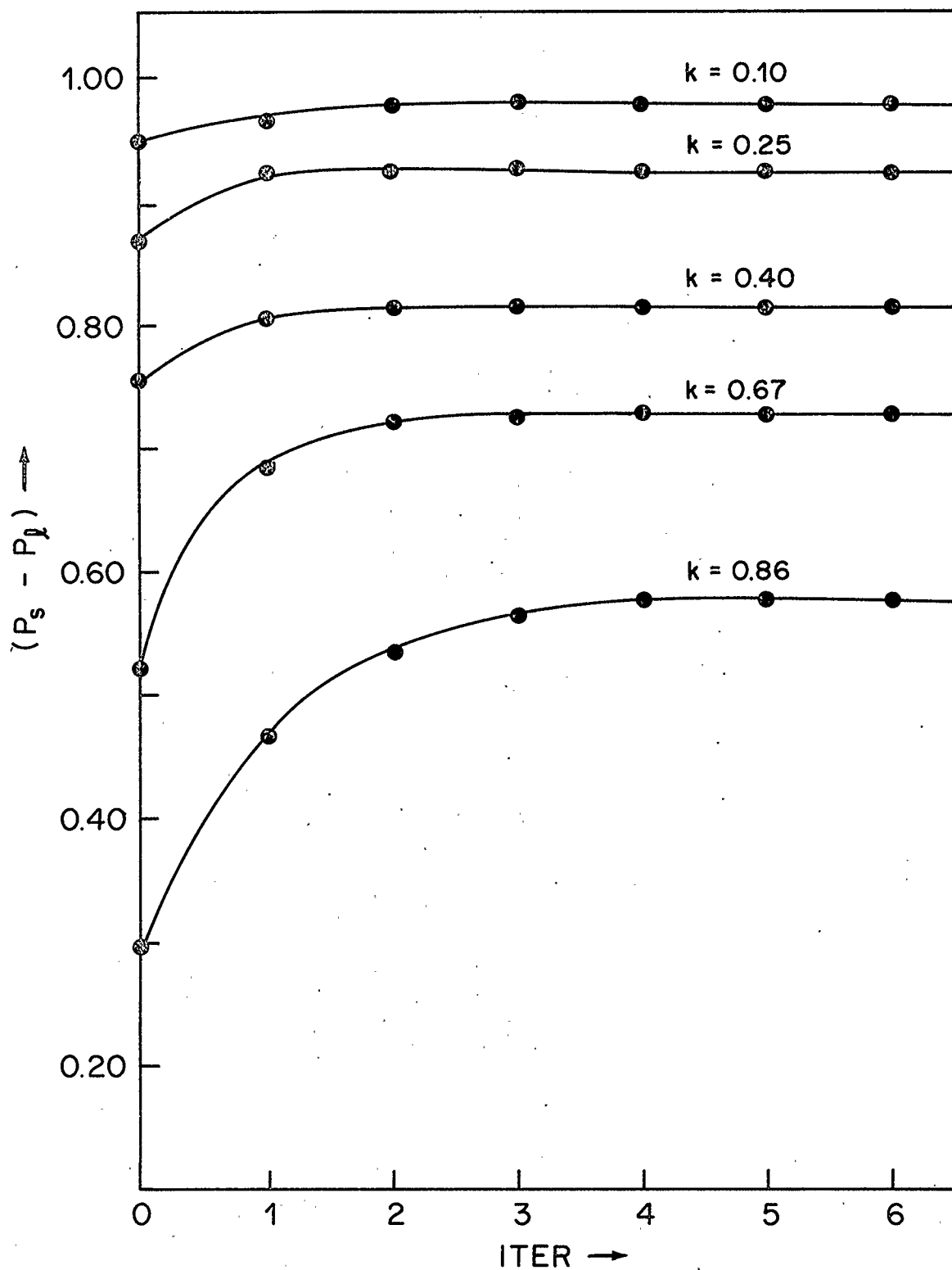


Figure 5.1: Dependence of the matrix elements,  $(P_s - P_l)$ , on the number of iterations, using the Salem's relation for different values of the bond alternation parameter.

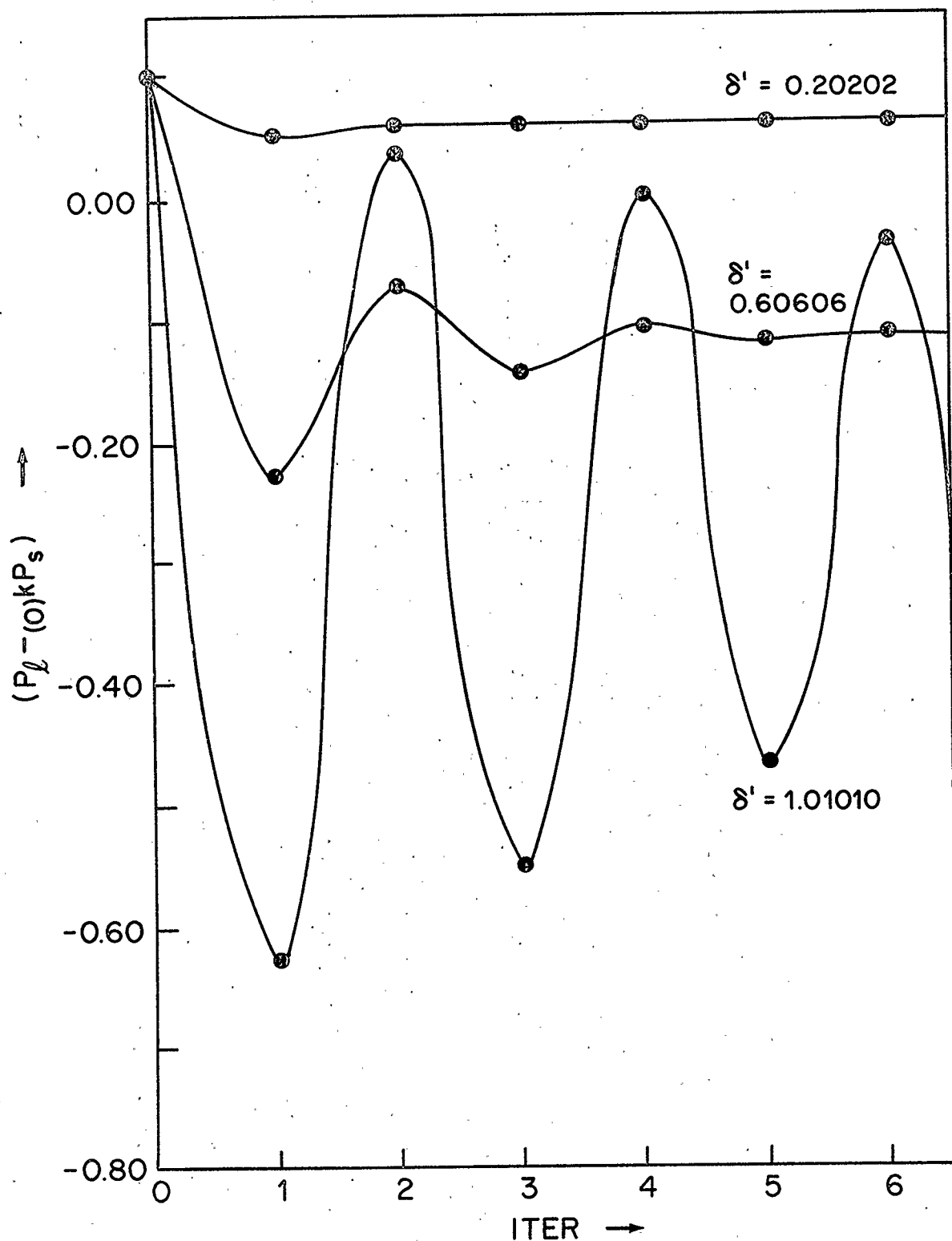


Figure 5.2: Dependence of the matrix elements,  $(P_l - (0)kP_s)$  on the number of iterations, using our relation for different delta values and the bond alternation parameter value,  $(0)k = 0.20202$ .

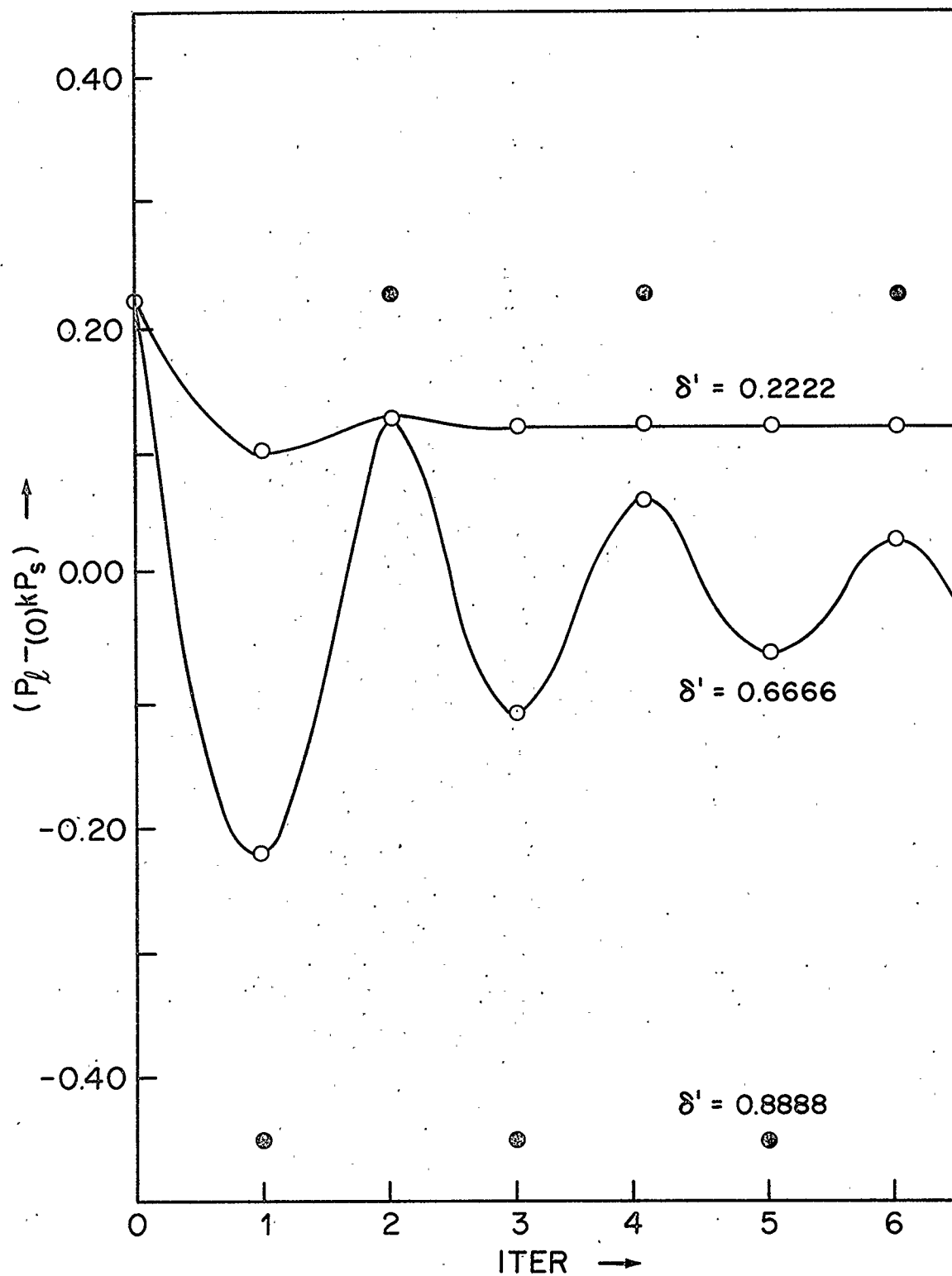


Figure 5.3: Dependence of the matrix elements on the number of iterations, using our relation for different delta values and the bond alternation parameter value,  $(0)k = 0.5556$ .

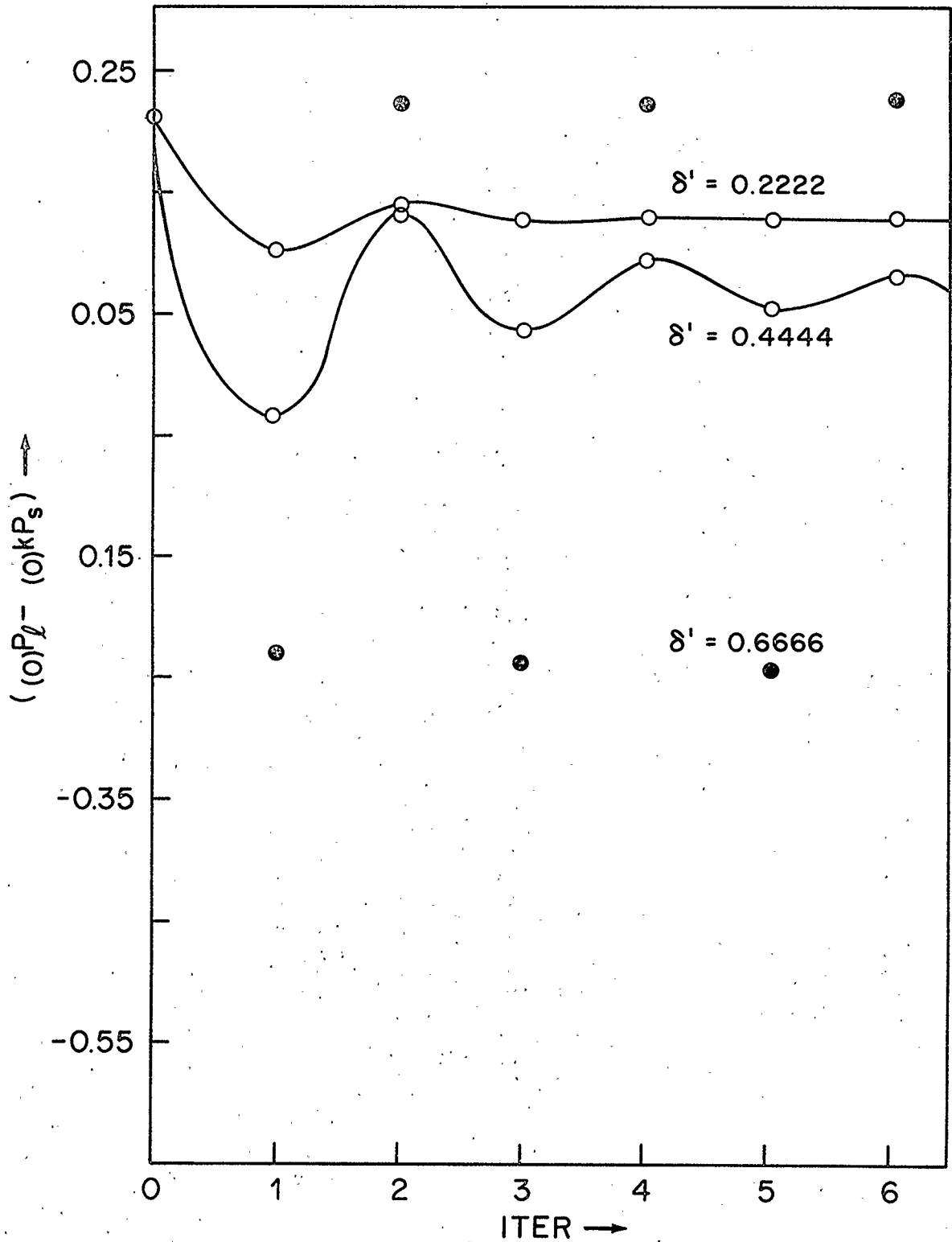


Figure 5.4: Dependence of the matrix elements,  $(P_l - (0)kP_s)$  on the number of iterations, using our relation for different delta values and the bond alternation parameter value,  $(0)k = 0.77778$ .

## CHAPTER 6

### APPLICATIONS

#### 6.1: INTRODUCTION

Although such analysis as was afforded by presentation of the previous three chapters has been one of the aims of this work, we have also been very much concerned with the applications of the iterative bond length method and the results thereof. To this end we carried out a number of calculations, all of which use the variational procedure (through Jacobi diagonalization) rather than perturbation theory to obtain the bond orders at each stage of the iteration. As indicated in section (2.2022) the first task in any application is to establish an appropriate  $\delta$  value. For this purpose, calculations of the bond lengths for a number of representatives of a given class (for example, polycyclic alternants) were carried out with several values of  $\delta$  to determine which value best reproduced the bond lengths obtained by experiment. Having established an appropriate

$\delta$  value, the bond lengths for other members of the class could be carried out. Even though the calculations were done for a large number of pi-electron systems, we will quote only a selected few as illustrative examples of the method. (A more exhaustive report from the point of view of applications has been published.<sup>41</sup>)

Both the 'analytical' method and the 'Jacobi diagonalization method' use the same relations to define the iterative scheme, and an investigation of this relation and the parameters chosen will also be considered in the following section.

## 6.20: NUMERICAL INVESTIGATIONS OF THE ITERATIVE METHOD

### 6.201: The Bond Length-Bond Order Relation

Essentially, the relations that are used are

$$({}_n)R_{rs} = \bar{a} - \bar{b} ({}_n)P_{rs} \quad (6-1)^\dagger$$

and

$$({}_n)H_{rs} = ({}_0)H_{rs} + \delta \left( ({}_{n-1})P_{rs} - P_{std} \right) \quad (6-2)^\dagger$$

Other relations that have been proposed<sup>20,42</sup> for pi-electron systems (alternant and non-alternant hydrocarbons) and that are an outcome of fitting the theoretically evaluated quantities,  $P_{rs}$ , and the experimentally determined quantities,  $R_{rs}$ , differ only in the values of  $\bar{a}$  and  $\bar{b}$ . For example, de Bruijn<sup>43</sup> has recently shown that a proper consideration of the effects of  $\pi$ -electron correlation suggests values of the coefficients of  $\bar{a}$  and  $\bar{b}$  which are different from those of the Coulson-Golebiewski relation.<sup>15</sup> [More recently, such relations have come under close scrutiny with the result that bond length relations which are either linear or quadratic in  $P$  have been suggested.<sup>43,44</sup>] However, since in the ensuing discussion on the characteristics of the iterative procedure, it appears that the bond length-bond order relation (R-P relation) does not in any respect alter the nature of our

†

conclusions, we would like to confine ourselves to a single relation, the Coulson-Golebiewski relation.

#### 6.202: The Choice of $\delta$ Values

The equation on which our iterative cycle rests is the (equation 2-6) relating the hamiltonian matrix element,  $H_{rs}$ , and the bond order element,  $P_{rs}$ . This can be considered as a truncated form of the Longuet-Higgins-Salem (LHS) relation to the first order excepting that the first order correction does not contain  $(0)H_{rs}$  explicitly. Clearly, in our relation (eq. 2-6) there is a 'variable' parameter,  $\delta$ , whose choice differs from one class of molecules (alternant hydrocarbons) to another (non-alternant hydrocarbons). Evidently, any rationalization of the choice of  $\delta$  can be made clear only if the nature of such bond order-bond length relations is understood. This is perhaps best approached through an investigation of the LHS relation.

#### 6.2021: The Longuet-Higgins-Salem Relation

Even though modifications of and explicit considerations of the  $\pi$ -electron interactions in the LHS approach have been made,<sup>43,45</sup> the original LHS approach is adequate for our task. (Their initial study is limited to cyclic polyenes.)

The total electronic energy is assumed to be given as the sum of two parts, one arising from the  $\sigma$  bonds and the other from the  $\pi$ -electrons.



$$T = E_{\sigma} + E_{\pi} \quad (6-3)$$

where  $E_{\sigma}$ , the  $\sigma$  electron energy, is assumed to be a sum of independent contributions from the C-C bonds:

$$E_{\sigma} = \sum_Q f(R_Q) \quad (6-4)$$

$R_Q$  is the length of the  $Q^{\text{th}}$  bond. The pi-electron energy,  $E_{\pi}$ , based on the L.C.A.O.-M.O. theory is given as a function of the bond integrals within the Hückel scheme.

$$E_{\pi} = E_{\pi}(H_1, H_2, \dots, H_Q, \dots) \quad (6-5)^{\dagger}$$

At equilibrium,

$$\left( \frac{\partial T}{\partial R_Q} \right)_{\text{equilibrium configuration}} = 0 \quad (6-6)$$

It can be shown<sup>(16)</sup> that

$$f'_Q + 2 P_Q H'_Q = 0 \quad (6-7)$$

where  $P_Q$  is the bond order of the  $Q^{\text{th}}$  bond;

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<sup>†</sup> The subscripts for H can be identified with the pair notation used in Chapter IV.

$$f'_Q = (df/dR)_Q \quad \text{and}$$

$$H'_Q = (dH/dR)_Q$$

As  $f'_Q$  and  $H'_Q$  only depend on the length  $R_Q$ , there is a relation between the bond length and the bond order. The relation that Longuet-Higgins and Salem adopted is

$$R_Q = 1.50 - 0.15 P_Q \quad (6-8)^{\dagger}$$

Furthermore, they assumed an exponential dependence of  $H_Q$  on  $R_Q$ :

$$H_Q = {}_{(0)}H_Q \exp \left( -(R_Q - R_{\text{std}})/a \right) \quad (6-9)^{\S}$$

Using equation (6-8), equation (6-9) can be written as

$$H_Q = {}_{(0)}H_Q \exp \left( 0.15(P_Q - P_{\text{std}})/a \right) \quad (6-9a)$$

They showed that the relation (6-9a) and the equilibrium condition given by (6-7) and (6-8) fix the function,  $f(R_Q)$ . From this it follows that the potential function for the C-C stretching modes of benzene (one member in the cyclic polyene taken for study) is

<sup>†</sup> The Coulson-Golebiewski (C.G.) relation <sup>15</sup>(equation 2.4) can be used and the value of ' $\xi$ ' obtained would be slightly different. ( $\xi$  (C.G.)  $\approx 0.58$ ).

<sup>§</sup> Other relations also have been proposed.<sup>20,43</sup>

determined by the constants ' ${}_{(0)}^H Q$ ' and ' $a$ '. This suggests that they can be evaluated from the known force constants for the  $A_{1g}$  and  $B_{2u}$  stretching modes.

Using the value for the totally symmetric,  $A_{1g}$ , and the totally asymmetric,  $B_{2u}$  stretching modes, they were able to obtain a value for ' $a$ ' of 0.3106.<sup>†</sup>

Clearly, this value of ' $a$ ' is dependent on the accuracy of the force field calculations of benzene. Longuet-Higgins and Salem made use of the force constants determined by Whiffen<sup>46</sup> Although consistent results have been reported for the force constant of the totally symmetric,  $A_{1g}$ , stretching mode,<sup>46,47</sup> a considerable amount of uncertainty prevails as regards the value for the totally asymmetric,  $B_{2u}$ , stretching mode.<sup>46,47</sup> This aspect can, in fact, be considered as a criticism against the use of one value of ' $a$ ' by Longuet-Higgins and Salem. Thus, it is clear that there exists a certain amount of arbitrariness in the value, ' $a$ '. Further, the value of ' $a$ ' evaluated by Longuet-Higgins and Salem may be reasonably appropriate for benzene but may be less appropriate for other molecules. One may in fact be better advised to determine ' $a$ ' as an average value for several molecules in a given class. This evaluation could, in principle, follow the LHS procedure. Alternatively ' $a$ ' may be obtained from comparison

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<sup>†</sup> The details of the evaluation are found in reference 16.

of experimental bond lengths and those calculated with various choices of 'a'.

As pointed out in section 2.2022, the relation given by equation (2-6) is a truncated version of the LHS  $(0)_{rs} H_{rs} / \xi$  replaced by a parameter,  $\delta$ . In our case  $\delta$  was selected on the basis of the best fit for the bond lengths of several molecules of one class. The value of  $\delta$  selected for the calculations of bond lengths of polynuclear aromatic hydrocarbons 0.45-0.50 is close to the value of 0.56 suggested by the results of Longuet-Higgins and Salem. The calculated results are in good agreement with the experimentally reported values for a wide range of molecules of this class. Further reference to these results will be given in section (6.203.)

A high delta value ( $\delta = 0.75$ ) reproduces experimental results for the linear polyenes - a different class of molecules. In the following section, we shall attempt a qualitative exposition of the need for different  $\delta$  values for the two classes.

#### 6.2022: $\delta$ Value for Polyenes

Although the  $\delta$  value required by our self-consistent procedure for condensed polycyclic alternant hydrocarbons is quite close to the  $\delta$  value predicted by Longuet-Higgins and Salem, there still exists a certain amount of arbitrariness in the values of  $\delta$ , appropriate to a particular class. One might expect that for molecules rather different from the above type,  $\delta$  could well take a different value. In particular, for linear

polyenes, which exhibit a marked bond alternation, the  $\delta$  value could well be different from that obtained for condensed systems.

Gouterman and Wagniere's work<sup>48</sup> sheds some light on this. Following Hobe and McLachlan's form<sup>44</sup> for  $f(R_Q)$ , they defined the total electronic energy in terms of the equilibrium bond lengths  $R_{\text{long}}$  and  $R_{\text{short}}$  for cyclic polyenes  $C_{18}H_{18}$ ,  $C_{24}H_{24}$  and  $C_{30}H_{30}$ . Gouterman and Wagniere<sup>48</sup> noticed that if 'a' is decreased (to 0.21 from 0.3106), there is a small trough in the potential curve for the asymmetric distortion. Hence, a lower value of 'a' could, in fact, lead to a stable asymmetric distortion, i.e. 'bond alternation'. (Several other workers<sup>49</sup> have also indicated that a low value of 'a' not only brings about bond alternation but also lowers the critical value of N (in  $C_{4N+2}H_{4N+2}$ ) at which the alternation occurs.)

Ignoring the end effects, one might consider the linear polyenes as behaving similarly to cyclic polyenes.<sup>†</sup> Hence, Gouterman and Wagniere's work suggests an increased  $\delta$  for linear polyenes with large N. Gouterman and Wagniere's value for 'a' of 0.21

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<sup>†</sup> However, in linear polyenes, the bond alternation always seems to be obtained in contrast to the critical N observed for the onset of alternation in cyclic polyenes.

corresponds to a  $\delta$  of 0.80, quite close to the  $\delta$  value of 0.75 which best reproduced experimental bond lengths using our procedure (see section 6.2031).

The increased  $\delta$  suggested by Gouterman and Wagniere's work on linear polyenes with large  $N$  and confirmed by us for finite polyenes clearly indicates a different sensitivity of  $H_Q$  to bond length changes. Just what the source of this different sensitivity is, less clear. It may in fact be a result of a combination of factors due basically to the "bond localization".<sup>§</sup>

We shall make further comments on the consequences of using larger values of  $\delta$  when the symmetry problem in the iterative calculation is discussed in Chapter 7.

#### 6.203: Applications

##### 6.2031: Alternant Hydrocarbons

The calculations for the bond lengths of alternant hydrocarbons were carried out for a wide range of  $\delta$  values to study

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<sup>§</sup> It might be worthwhile pointing out that the "localization" model as proposed by Dewar and Schmeising<sup>21</sup> to explain the physical and chemical properties appears to work well for finite polyenes. Vibrational spectroscopic studies coupled with force field calculations by Popov and Kogan<sup>50</sup> on trans-butadiene and trans-hexatriene also seem to indicate that the localization model in contrast to the delocalization model is appropriate.

the sensitivity of the iterative procedure to  $\delta$  values and to enable us to choose the  $\delta$  value for which the experimental results are best reproduced. As regards the sensitivity, the convergence slows down with an increase in the  $\delta$  value. The  $\delta$  value of 0.45 appears to be the appropriate value.

With this  $\delta$  value the iterative bond length procedure was applied to a number of condensed polycyclic systems of interest for which the experimental bond lengths have not been reported. Since a compilation of our results has been published,<sup>41</sup> we indicate the results for only a few systems in Table 6.4.

Similarly, to illustrate the validity of using a higher  $\delta$  value for linear polyenes, we give the results for butadiene and hexatriene in Table 6.3. Again having established the appropriate  $\delta$  value for this class we applied the method to systems for which experimental data had not been published.

#### 6.2032: Non-alternant Hydrocarbons

The success of this simple iterative procedure as indicated by comparison of the results in Table 7.1 prompted an extension to non-alternant systems. The extension is hampered by the fact that experimental bond length data for a wide variety of non-alternant hydrocarbons are not available. Further, in contrast to alternants where the charge density on all centers is unity (both in Hückel and in the SCF-ZDO representation), for non-alternants, the charge varies from center to center. Hence, in addition to self-consistent bond orders, a self-consistent charge distribution on

centers should be attempted.

The first difficulty was circumvented by selecting a few non-alternant hydrocarbons which belong to a class of strained systems. Since the experimental data<sup>†</sup> are available for these systems (for example, acenaphthylene,<sup>51a</sup> acepleiadylene,<sup>51b</sup> 3,4-dimethylene-cyclobutene<sup>51c</sup> and fulvene<sup>51d</sup>), hopefully one could make a meaningful choice of  $\delta$ . The  $\delta$  value so obtained may not be appropriate for other classes of non-alternant hydrocarbons.

The second difficulty is set aside on the grounds that a one parameter procedure in iterative calculations is more tractable.<sup>§</sup> Perhaps more to the point, for the strained non-alternants that can be checked, the perturbation of the off-diagonal hamiltonian matrix elements seems to be sufficient in that the results are in agreement with those obtained by experiment (see Table 6.2). The value of  $\delta$  which best represented the bond lengths that could be checked against experimental data is 0.75.

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<sup>†</sup> The crystal structure studies were not made on the free molecules. The derivatives of acenaphthylene and the TNB complex of acepleiadylene were used for the crystal structure studies.<sup>51a,51b</sup>

<sup>§</sup> Further Binsch, Heilbronner and Murrell<sup>32</sup> point out that in bond fixation studies on pentalene the variation of the coulomb integral does not affect the bond lengths results.



### 6.30: FURTHER REMARKS ON THIS ITERATIVE PROCEDURE

#### 6.301: Effect of Choice of Standard Bond Length

Hitherto, our discussion has been limited to the bond length-bond order relation and the choice of  $\delta$  values. In addition to this we should point out that the value assigned to  $P_{std}$  is important. Clearly, variation of  $P_{std}$  will affect the way in which a given  $\delta$  value perturbs the core element  $H_{rs}$  in  $H_{rs}' = \beta^0 - \delta P_{std}$  and, as such, changes the relation between the core element and the term  $\delta P_{rs}$  in the iterative procedure. Clearly, the choice of  $\delta$  appropriate to a given class depends on the selection of  $P_{std}$ . In addition, changes in  $P_{std}$  can either slow down or hasten the convergence. The  $P_{std}$  value used in our calculation is unity, corresponding to the bond order of ethylene. Although some calculations were carried out for the benzene value of  $P_{std} = 0.667$ , no significant differences were apparent.

#### 6.302: Loss of Symmetry

We might also remark that normally at all stages of iteration the symmetry is preserved. When  $\delta$  values of unity were used in our calculations all systems tested reduced to a set of linked ethylenic structures. In some instances such reduction brings with it a reduction to a kekulé, e.g. naphthalene goes to such a structure. The original symmetry of linear polyenes

undergoes no change. Since  $\delta$  values of unity reduce the core element to zero this result is consistent with the results obtained by Paldus and Cizek.<sup>53</sup> Somewhat more intriguing was the observation that for certain values of  $\delta < 1$ , e.g. calculations on pentalene and heptalene, which belong to the class of (strained) non-alternants, indicate that the starting symmetry is lowered after several iterations and the self-consistent results obtained correspond to the lower symmetry. In Chapter 7 we shall discuss this symmetry 'dilemma', with particular reference to pentalene and heptalene.

#### 6.303: On Uniqueness of the Iterative Solution

In addition to the "loss of symmetry" problem, the question of uniqueness of the  $n^{\text{th}}$  iterated form in those cases where the symmetry is maintained should also be considered. For example, when iterative bond length calculations on naphthalene are carried out using the same Hückel matrix but for two arbitrary but different initial bond order matrices, the same  $n^{\text{th}}$  iterated bond order is obtained. The uniqueness of those cases in which there is also a symmetry loss will be mentioned in Chapter 7.

TABLE: 6.1

SELF-CONSISTENT CALCULATIONS OF BOND LENGTHS (Å)

POLYCYCLIC AROMATIC HYDROCARBONS

Molecule	Bond <sup>a</sup>	The Present Method	Experimental <sup>†</sup> Values
Naphthalene (I)	1-2	1.381	1.363
	2-3	1.415	1.415
	1-9	1.421	1.421
	9-10	1.418	1.418
Benz(c)phenanthrene (II)	1-2	1.385	1.378
	2-3	1.411	1.409
	3-4	1.385	1.374
	4-16	1.416	1.391
	5-6	1.374	1.352
	6-17	1.430	1.430
	5-16	1.430	1.443
	14-15	1.433	1.446
	1-15	1.415	1.433
	14-17	1.405	1.412
	15-16	1.415	1.431

<sup>a</sup> Bond numbering according to "Ring Index" (American Chemical Society, 1960);  $\delta$  value, 0.45 is used for the calculation of the bond lengths.

<sup>†</sup> See reference 17.

TABLE: 6.2

SELF-CONSISTENT BOND LENGTH RESULTS IN Å UNITS

STRAINED SYSTEMS

Molecule	Bond	This Work	Experimental * Result
3,4-dimethylenecyclobutene	1-2	1.485	1.488 ± 0.009
	1-4	1.343	1.357 ± 0.005
	2-3	1.488	1.516 ± 0.020
	2-5	1.342	1.335 ± 0.003
Fulvene	1-2	1.345	1.340 ± 0.006
	1-5	1.480	1.476 ± 0.008
	2-3	1.477	1.462 ± 0.009
	5-6	1.345	1.347 ± 0.010
Acenaphthylene	1-2	1.346	-
	2-10	1.476	1.478 <sup>s</sup>
	10-12	1.437	1.414
	3-10	1.372	1.363
	3-4	1.432	1.463
	4-5	1.368	1.368
	5-11	1.435	1.396
	11-12	1.395	1.406

TABLE: 6.2 cont'd

SELF-CONSISTENT BOND LENGTH RESULTS IN Å UNITS  
STRAINED SYSTEMS

Molecule	Bond	This Work	Experimental * Result
Acepleiadylene	1-2	1.418	1.399 <sup>†</sup>
	1-11	1.382	1.383
	2-12	1.382	1.406
	3-12	1.469	1.444
	3-4	1.349	1.356
	4-5	1.470	1.427
	9-10	1.350	1.364
	10-11	1.469	1.457
	11-15	1.430	1.424
	12-16	1.430	1.456
	15-16	1.405	1.395

<sup>§</sup> Ref. 51. The data given in Table 6.2 correspond to the molecule, acenaphthoquinone. Only mean values are quoted.

<sup>†</sup> Ref. 52. The experimental results indicated in Table 6.2 correspond to acepleiadylene in its complex state with 1,3,5-trinitrobenzene.

\* See reference 41.

TABLE: 6.3

SELF-CONSISTENT BOND LENGTH RESULTS IN Å UNITS

LINEAR POLYENES

Molecule	Bond	This Work	Experimental <sup>†</sup> Result
Butadiene	1-2	1.341	1.337 ± 0.005
			1.339
	2-3	1.481	1.483 ± 0.01
			1.480
Hexatriene	1-2	1.341	
	2-3	1.479	
	3-4	1.345	
Octatetraene	1-2	1.341	
	2-3	1.479	
	3-4	1.345	
	4-5	1.477	

<sup>†</sup> See reference 17.

TABLE: 6.4

SELF-CONSISTENT BOND LENGTH RESULTS IN Å UNITS

Molecule	Bond	The Present Work	Literature <sup>†</sup> Value
Dibenzo(def, mno)chrysene	1-2	1.440 <sup>§</sup>	
	1-18	1.367	
	2-3	1.393	
	2-20	1.431	
	3-4	1.420	
	4-5	1.416	
	4-22	1.423	
	5-6	1.390	
	6-7	1.404	
	7-8	1.401	
	8-9	1.439	
	8-22	1.423	
	20-21	1.415	
	21-22	1.420	
Benz(e)azulene	1-2	1.380 <sup>*</sup>	1.383
	1-14	1.418	1.415
	2-3	1.417	1.413
	3-4	1.381	1.382

TABLE: 6.4 cont'd

SELF-CONSISTENT BOND LENGTH RESULTS IN Å UNITS

Molecule	Bond	The Present Work	Literature <sup>†</sup> Value
	4-5	1.417	1.416
	5-6	1.469	1.446
	5-14	1.392	1.405
	6-7	1.350	1.362
	7-8	1.470	1.448
	8-9	1.355	1.374
	8-12	1.476	1.448
	9-10	1.465	1.430
	10-11	1.350	1.370
	11-12	1.469	1.439
	12-13	1.355	1.374
	13-14	1.465	1.445
Benz(f)azulene	1-2	1.381 <sup>*</sup>	1.394
	1-14	1.416	1.414
	2-3	1.416	1.411
	3-4	1.381	1.384
	4-5	1.417	1.413
	5-6	1.467	1.446



TABLE: 6.4 cont'd

SELF-CONSISTENT BOND LENGTH RESULTS IN Å UNITS

Molecule	Bond	The Present Work	Literature <sup>†</sup> Value
	5-14	1.392	1.405
	6-7	1.351	1.366
	7-8	1.464	1.437
	8-9	1.356	1.377
	9-10	1.467	1.438
	9-13	1.476	1.464
	10-11	1.351	1.370
	11-12	1.464	1.431
	12-13	1.355	1.373
	13-14	1.469	1.451

<sup>†</sup> See reference 41.

## CHAPTER 7

### THE "STABILITY" PROBLEM

#### 7.10: INTRODUCTION

In the last chapter, we pointed out that there is a lowering of symmetry for pentalene and heptalene when the iterative procedure is carried out for particular delta values. This prevails whether the starting symmetry is  $D_{2h}$  or  $C_{2v}$ . Thus, for example, we observed that for the initial  $D_{2h}$  symmetry, the final one is  $C_{2h}$  and for  $C_{2v}$ , it is  $C_s$ . In section 7.20 we shall discuss this symmetry "breakdown".

In all our calculations on pentalene and heptalene, the structure belonging to the lower symmetry group is a bond-alternating structure. The instability of the higher point group is an example of "lattice instability". This instability has been examined by Nakajima and his coworkers<sup>54</sup> and den Boer<sup>55</sup> for pentalene and heptalene from the point of view of "nuclear perturbation" and they too found the alternating structure to be of lower energy.

Associated with the symmetry problem but more general than lattice instability is the "singlet" instability of the Hartree-Fock solution.<sup>2,52</sup> It has been observed by Paldus and Cizek<sup>2,53</sup> that where this "instability" has occurred, the alternative stable solution is found to belong to a lower symmetry and for

cyclic polyenes, this is a bond alternating structure.

Recalling the parallel between the iterative Hückel scheme and the SCF-ZDO scheme, as given in Chapter 3, it might be said that an increase in  $\delta$  value corresponds to a lowering of the matrix element  $(0)H_{rs}$  with a concomitant increase in the perturbation,  $\delta P_{rs}$ . In the SCF-ZDO scheme, this is similar to lowering the value for the core integrals  $|\bar{H}_{rs}|$  such that the contribution of the "exchange" term,  $-\frac{1}{2} P_{rs} \gamma_{rs}$ , is relatively larger.

Paldus and Cizek,<sup>58</sup> in their study of the "singlet" instability of the Hartree-Fock solutions of cyclic polyenes, analysed the influence of the "coupling constant",  $\lambda$ , where  $\lambda$  is the ratio of the repulsion integrals,  $\gamma_{rs}$ , to the core integral,  $\bar{H}_{rs}$ , on the "stability". They observed the "singlet" instability setting in for high values of  $\lambda$ , corresponding to small values of  $\bar{H}_{rs}$ .

Our observation that for a high value of  $\delta$ , "lattice instability" occurs setting in for pentalene and heptalene is of course equivalent to an instability for low values of  $\bar{H}_{rs}$  relative to what appears to be a high exchange contribution. However, it was not clear whether this meant that pentalene and heptalene would in fact show the "singlet" instability as defined by Paldus and Cizek.

So far, no attempt has been made to study the "stability" of the HF solution of pentalene and heptalene. We shall state the "stability" conditions and examine the nature of the HF solution for these systems in section 7.30.

## 7.20: THE SYMMETRY CONSIDERATIONS

### 7.201: The Symmetry 'Dilemma' in the Present Iterative Method

Numerical investigations using the present iterative procedure indicate<sup>†</sup> that for small perturbations,  $0 < \delta < 0.40$ , the symmetry ( $D_{2h}$ ) is conserved for pentalene. For  $0.40 < \delta < 1.0$ , there is a slow "change-over" from the high symmetry to the low symmetry (for example, if the high symmetry is  $D_{2h}$ , the low is  $C_{2h}$ , if it is  $C_{2v}$ , then the low one is  $C_s$ ; see Tables 7.1 and 7.3). Furthermore, the convergence rate for the lower symmetric case, once the change-over has occurred, increases with an increase in the  $\delta$  values.

For pentalene, the low symmetry configuration exhibits bond alternation around the periphery (in  $C_{2h}$ ) or within a ring (in  $C_s$ ). At  $\delta = 1$ , the iterative cycle leads to an essentially alternating single bond and double bond structure. (For  $\delta > 1$ , "non-physical" density matrix elements result.) The same comments can be made for heptalene - see Table 7.4.

The loss of symmetry might be ascribed to the cumulative effect of the random error that occurs at each stage of the iteration. To investigate this, numerical computations were repeated in double

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<sup>†</sup> These observations are based on 100 iterations.

precision format, the higher symmetry is lost for  $\delta$  values greater than 0.4 but at a much slower rate.

It would appear that the rounding error on even the first iteration produces a representation of the hamiltonian which does not preserve symmetry exactly, i.e. in the case of single precision calculations symmetry is not preserved beyond, say, the seventh figure, even at the first iteration. Such symmetry loss is not important in cases where the energy surface is concave to the symmetry loss since subsequent iterations and their attendant random errors will always return to the original symmetry. However in those cases, such as for pentalene with  $\delta > 0.4$ , where the energy surface is not stable to symmetry loss this initial loss of symmetry may produce on the next iteration a slightly more asymmetric solution and this procedure will continue until the energy surface (in the new symmetry) is stable to the random error symmetry loss.

In other non-alternants, azulene ( $C_{2v}$ ), as-indacene ( $C_{2v}$ ) and dibenzpentalene ( $C_{2v}$ ), lowering of symmetry occurs only at high  $\delta$  values ( $\delta = 0.8$ ). For the latter two, the  $\lambda^{\max}$  value is equal to or greater than the critical  $\lambda_{\max}$  predicted by Binsch, Heilbronner and Murrell<sup>32</sup> whereas for azulene it is somewhat less ( $\lambda^{\max} = 1.26$  vs 1.8 for  $\lambda_{\text{crit}}^{\max}$ ).

To investigate if this 'lowering' of symmetry is characteristic of all non-alternant hydrocarbons or not, we repeated the calculations for two model systems (see Table. 7.4) where the largest

eigenvalue of their polarizability matrix is much smaller than the critical value.<sup>32</sup> For both systems, the initial symmetry is preserved (see Table 7.4).

#### 7.202: The Onset of Symmetry Loss

According to Binsch, Heilbronner and Murrell,<sup>32</sup> for molecules for which the largest eigenvalue of the polarizability matrix,  $\pi$ , exceeds a "critical" value, a second order bond distortion leading to stability of a lower symmetry is not unexpected. The systems, pentalene, heptalene, as-indacene and dibenzopentalene were indeed investigated in view of the fact that the largest eigenvalue of the bond-bond polarizability matrix of these systems is equal to or greater than Binsch's "critical" value of  $1.80 \beta^{-1}$ . For pentalene and heptalene, the largest eigenvalue of the polarizability matrix is greater than the critical value,  $1.80 \beta^{-1}$ , by a wide margin. These are the same systems which experience lowering of symmetry in our iterative calculations, even for relatively small values of  $\delta$  (i.e. down to  $\delta = 0.4$ ).

The importance of the eigenvalues of the polarizability matrix,  $\pi$ , to the iterative procedure may be made clearer by recalling the eigenvalues of the  $\delta \underline{A} \underline{E} \underline{A}^\dagger$  should be less than unity for convergence of the iterative procedure. This is tantamount to saying that the largest eigenvalue of  $\delta \underline{A} \underline{E} \underline{A}^\dagger$  should be less than unity. Clearly, to realize "physically interpretable" density matrix elements,  $\delta$  should be less than 1. For pentalene, the largest eigenvalues of the polarizability matrix are 2.36 and

2.57<sup>s</sup> respectively, thus requiring a small  $\delta$  value.

Naphthalene, as-indacene and dibenzpentalene have eigenvectors equal to or less than the "critical" value (see Table 7.1) and this suggests that  $\delta$  values which caused loss of symmetry in pentalene and heptalene would not result in a symmetry loss - just as observed in the present study. However, for high  $\delta$  values, i.e.  $\delta > 0.8$ , these systems would also exhibit instability.

#### 7.203: Non-analyticity

From the numerical investigation outlined, there appears to be a relation between  $\lambda_P^{\max}$ , the value of  $\delta$ , and the onset of the loss of symmetry using the iterative method with a variational solution of the representation for each iteration. No definitive statement of the relation has been forthcoming. Although no direct comparison with the aforementioned numerical results can be made, it will be recalled that the perturbation result even in first order, is stable only if the matrix  $(\underline{1} - \delta \underline{A} \underline{E} \underline{A}^\dagger)$  is non-singular and converges only if the eigenvalues of  $\underline{A} \underline{E} \underline{A}^\dagger$  are of a magnitude less than  $1/\delta$ . Clearly such conditions may be violated and become pathological, even non-analytic, at  $\delta \lambda^{\max} = 1$ . This is of course somewhat similar to the non-analyticity observed by Paldus and Cizek.<sup>57</sup>

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<sup>s</sup> See Table 3.1. The eigenvalues are of course dependent on parametrization and higher values have been reported.

### 7.30 : STABILITY

#### 7.301 : The Hartree-Fock Stability Conditions

Paldus and Cizek<sup>53</sup> have reviewed the importance of the stability of the Hartree-Fock solutions for the closed- and the open-shell cases. They applied "stability" conditions (to be stated in the following section) to the HF solutions of cyclic polyenes, linear polyacenes and odd polyene radicals.

Since the theory of the stability of Hartree-Fock states is fairly well-known,<sup>54,55</sup> we will not dwell at length on it. Instead, we shall introduce the stability conditions for the closed shell systems directly and apply them to Hartree-Fock solutions of pentalene and heptalene.

The variation of the energy functional

$$E(\Phi) = \langle \Phi | \hat{H} | \Phi \rangle / \langle \Phi | \Phi \rangle$$

is zero for the Slater determinant of the Hartree-Fock orbitals. This stationary point, that the functional  $E(\Phi)$  represents, can be either a minimum, a maximum or a saddle point in the functional space. In order to distinguish between these alternatives, it is necessary to examine the second variation of the energy functional,  $\delta^2 E(\Phi)$ . Thouless,<sup>54</sup> Fukuda and Sawada<sup>55</sup> and others<sup>56</sup> defined the "stability" condition within the variational space considered as requiring  $\delta^2 E(\Phi)$  to be positive for a "stable" solution. This condition ensures that



the HF single determinant represents a local minimum of the energy functional.

### 7.302 : The "Singlet" Stability Conditions

In the case of the singlet stability problem, the variational space is spanned by single determinant functions with doubly occupied orbitals, i.e. by the Slater determinants which are singlet eigenfunctions of the operator  $\hat{S}^2$ .

To formulate the singlet stability conditions, the hamiltonian of the closed-shell  $2n$  electronic system is written as a sum of one- and two-particle operators  $\hat{h}_\mu$  and  $\hat{v}_{\mu\nu}$  respectively.

$$\hat{H} = \sum_{\mu} \hat{h}_{\mu} + \sum_{\mu < \nu} \hat{v}_{\mu\nu} \quad (7-1)$$

Defining  $\Psi_1, \Psi_2 \dots$  etc. as the HF molecular orbitals where the first  $n$  orbitals ( $\Psi_1, \Psi_2 \dots \Psi_n$ ) are occupied in the ground state,  $|\Phi_0\rangle$ , the HF solution within a normalization constant is written as

$$|\Phi_0\rangle = \det ||\Psi_1 \bar{\Psi}_1 \Psi_2 \bar{\Psi}_2 \dots \Psi_n \bar{\Psi}_n|| \quad (7-2)$$

where the bar indicates the spin  $\beta$  and no bar denotes the spin  $\alpha$ . One can then consider an arbitrary function,  $|\Phi\rangle$ , which is not orthogonal to  $|\Phi_0\rangle$  and which lies in the neighbourhood of  $|\Phi_0\rangle$  :

$$|\Phi\rangle = |\Phi_0\rangle + \sum_{i=1} |\Phi_i\rangle \quad (7-3)$$

where  $|\Phi_i\rangle$  is given, according to the equation 4 of Ref. 2

as

$$|\Phi_i\rangle = (i!)^{-1} \sum_{U_1, U_2, \dots, U_i} \left( \sum_{j=1}^i d_{U_j} \right) |U_1, U_2, \dots, U_i\rangle \quad (7-4)$$

$d_{U_j}$  refer to the mixing coefficients which denote the weights with which the virtual orbitals are admixed to the occupied orbitals;  $|U_1, U_2, \dots, U_i\rangle$  denotes the determinantal function which is obtained from  $|\Phi_0\rangle$  by replacing the occupied spin orbital by the virtual orbital  $i$ .

The energy of  $\hat{H}$  in  $|\Phi\rangle$  is

$$E(\Phi) = \langle \Phi | \hat{H} | \Phi \rangle / \langle \Phi | \Phi \rangle \quad (7-5)$$

and the second variation in energy up to second order is defined as  $E(\Phi) - E(\Phi_0)$ . It can be shown<sup>2</sup> that if this variation of the energy is to be positive, then the eigenvalues of the characteristic value problem

$$\begin{bmatrix} \mathbf{A}^S & \mathbf{B}^S \\ \mathbf{\bar{B}}^S & \mathbf{\bar{A}}^S \end{bmatrix} \begin{bmatrix} \mathbf{D}^S \\ \mathbf{\bar{D}}^S \end{bmatrix} = \lambda \begin{bmatrix} \mathbf{D}^S \\ \mathbf{\bar{D}}^S \end{bmatrix} \quad (7-6)$$

must be positive.<sup>†</sup> Here, the elements  $A_{U_1, U_2}$  and  $B_{U_1, U_2}$  that constitute the square matrices  $\underline{A}^S$  and  $\underline{B}^S$  are essentially the matrix elements of the hamiltonian given in (7-1) between the monoexcited states and between the ground and biexcited states:

$$A_{U_1, U_2} = \langle U_1 | \hat{Q} | U_2 \rangle \quad (7-7a)$$

and

$$B_{U_1, U_2} = \langle U_1 U_2 | \hat{Q} | \Phi_0 \rangle \quad (7-7b)$$

where the  $\hat{Q}$  operator is  $\hat{H} - E(\Phi_0)$ . The  $\underline{D}^S$  are made up of the mixing coefficients,  $d_{U_j}$ .  $\lambda$  refers to the eigenvalue.

When the matrices  $\underline{A}^S$  and  $\underline{B}^S$  are real matrices, the "singlet" stability may be further simplified to

$$(\underline{A}^S + \underline{B}^S) \underline{D}^S = \lambda^S \underline{D}^S \quad (7-8)$$

However, it is equation (7-6) that we used to examine the singlet stability of the Hartree-Fock solution for pentalene and heptalene. Further, in the evaluation of the matrix elements of  $\underline{A}$  and  $\underline{B}$ , no symmetry restrictions were involved.

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<sup>†</sup> Since the derivation of (7-6) is fairly well-documented in literature, (see equations 1 - 14 for the derivation in the coordinate space representation of Ref. 2 ) we omit it here.

### 7.303: The Method of Calculations

Our concern is primarily with pentalene and heptalene, however the calculations were also extended to the higher homologs of  $C_{4N}H_{4N}$  which belong to the symmetry group,  $D_{2h}$ . The HF calculations were carried out within the Pariser-Parr-Pople scheme, assuming the ZDO approximation.<sup>§</sup>

The calculation was set up assuming that all carbon-carbon neighbour bond distances were identical ( $1.397 \text{ \AA}$ ). The one- and two-particle integrals over the carbon  $2p_z$  orbitals were determined using both the "theoretical" parametrization and the Pariser-Parr parametrization which consider  $\sigma$  electron screening and correlation in different ways - a factor in terms of which instability has been analysed.<sup>45,57</sup>

In M.O. calculations,  $\sigma$  electron screening and correlation effects may be absorbed, in part, in the semi-empirical values of the coulomb repulsion integrals. For example, the one centre repulsion integral  $\gamma_{rr}$  in the PPP scheme is of the order of 11 e.v. whereas in the theoretical "parametrization" the same integral takes the value of 17.23 e.v. The remaining two centre repulsion integrals, in the two schemes, show a similar disparity. Consequently use of the two schemes and comparison of the results

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<sup>§</sup> The conclusions on the stability study are restricted by this approximation.

allows some assessment of correlation effects.

7.3031: Theoretical "Parametrization"

The repulsion integrals are calculated with the analytical expressions for the repulsion integrals obtained using  $2p_z$  atomic orbitals, with the effective nuclear charge  $Z = 3.2358$ . We assumed the orthogonality of the individual orbitals. (It is by no means correct to omit the overlap in this case; however, Paldus and Cizek<sup>58</sup> found that the inclusion of overlap did not materially change their conclusions. Assuming that this is valid in our case, too, and recognizing that the neglect of overlap simplifies the calculation, we have followed the above parametrization.) Following Ruedenberg, the core integrals in the off-diagonal element are taken as  $\bar{\beta} = -3.7163$  e.v.

7.3032: The Pariser-Parr "Parametrization"

In the PPP representation the two centre coulomb repulsion integrals  $\gamma_{rs}$  are calculated using the charged-sphere approximation with Slater's effective nuclear charge value of  $Z = 3.25$ . The one centre coulomb repulsion integral,  $\gamma_{rr}$ , is taken as 11.0 e.v. The core integral ( $\bar{\beta}$ ) is given the value  $\beta = -2.39$  e.v.

### 7.304: The Matrix Elements of the Stability Equation

In order to examine the "singlet" stability of the HF solution for pentalene and heptalene obtained using the two "parametrization" schemes, the matrix elements  $A_{U_1, U_2}^S$  and  $B_{U_1, U_2}^S$  appearing in the characteristic-value problem (equation 7-6) must be evaluated. As indicated in the section 7.20, these matrix elements are the matrix elements of the hamiltonian (7-1) between the monoexcited states and between the ground and biexcited states.

For convenience, we shall denote the singly excited configuration by  $\begin{vmatrix} j \\ i \end{vmatrix}$  (as against  $|\Phi_0\rangle$  for the ground state configuration) and the double excited configuration by  $\begin{vmatrix} j & l \\ i & k \end{vmatrix}$ . The occupied orbitals from which the excitation occurs are denoted by  $i$  and  $k$  and the virtual orbitals at which the excitation terminates are given the symbols  $j$  and  $l$ .

### 7.3041: The Truncation on the Set of Excitations

For pentalene and heptalene we consider only the excitations involving the two highest occupied levels and the two lowest virtual levels. In particular, we carried out the calculations for two sets of excitations.

- (a) All the possible monoexcited state configurations and the biexcited state configurations arising out of the excitations  $i(n) \rightarrow j(n+1)$ ;  $i(n) \rightarrow j(n+2)$  and  $i(n-1) \rightarrow j(n+1)$ .

- (b) In addition to the excitations considered in (a), we included the excitation  $i(n - 1) \rightarrow j(n + 2)$ .

The 'n' in parenthesis indicates the total number of the occupied levels. The characteristic value problems are solved within the type of excitations described in (a) and (b). We shall present the results of the calculations for pentalene and heptalene in section 7.40.

#### 7.3042: The Effect of the Variation of the "Coupling" Constant, $\Lambda$

In section 7.10 we indicated the studies carried out by Cizek and Paldus<sup>53</sup> on the use of the "coupling" constant,  $\Lambda$ , in examining the stability problem. The variation of the "coupling" constant can be brought about by varying the value of the core integral,  $\bar{H}_{rs}$ , alone without recourse to an adjustment of both the core integral and the repulsion integral,  $\gamma_{rs}$ . Following this approach, we solved the characteristic value problem for several values of the core integrals at both levels of truncation, i.e. for both (a) and (b) above.

We shall consider the results obtained in the following section and discuss their implications.

#### 7.40: RESULTS AND DISCUSSION

Clearly, an examination of the lowest eigenvalue of the

characteristic value problem (equation 7.8 ) would indicate whether the Hartree-Fock solution obtained for pentalene and heptalene within the schemes explained in section 7.3 is stable or not. As the results indicate (see Tables 7.5 & 7.6), all the eigenvalues are positive in both schemes when the standard value of  $\bar{H}_{rs}$ , of the core integral is used. This suggests that the Hartree-Fock solution with the above parametrization is "singlet" stable.

When the core integral,  $\bar{H}_{rs}$ , is varied systematically, the results (Tables 7.5 and 7.6) show that the lowest eigenvalue is negative for small values of  $\bar{H}_{rs}$  in both the "theoretical" parametrization scheme and the "PPP" scheme. However, there is a definite accentuation of the negative value in the "theoretical" parametrization scheme in comparison with the PPP scheme. This is due to the fact that the inter-electronic repulsion is smaller at short distances in the PPP scheme than in the "theoretical" scheme. Cizek and Paldus have made a similar observation<sup>53</sup> in their study on cyclic polyenes.

The appearance of the negative eigenvalue for small  $\bar{H}_{rs}$  clearly indicates that the HF solution is unstable. From the plots of the lowest eigenvalue against the core integral,  $\bar{H}_{rs}$ , it can be said that the "instability" occurs at a higher value of  $\bar{H}_{rs}$  in the "theoretical" parametrization scheme relative to the PPP parametrization scheme. The reasoning is the same as the one given above to account for the accentuation of the negative eigenvalue.



Another aspect that can be extracted from this study is that the magnitude of the lowest eigenvalue is dependent on the maximum value considered for the quasimomentum transfer (see Tables 7.5 and 7.6). In our problem, this is equivalent to comparing the results obtained for the descriptions (a) and (b) given in section 7.3041. As we go from (a) to (b), it is observed for pentalene and heptalene that the magnitude of all the eigenvalues, including the lowest eigenvalue, goes up.

In our investigations, however, we noticed that the magnitude of the eigenvalues of the characteristic value problem in heptalene is smaller than that in pentalene and that of the higher homolog, nonalene, is smaller than that of heptalene. This is quite interesting since in the analysis carried out by Paldus and Cizek<sup>53</sup> and Tric<sup>52</sup> for polyenes, the tendency towards "instability" increases as the dimensionality,  $N$ , of the basic unit  $C_{4N+2}H_{4N+2}$  increases. However, for small values of the 'coupling' constant, i.e. approximately standard core integral values, the trend observed by Paldus and Cizek is, indeed, found.

#### 7.401: On Uniqueness of the Self-consistent solution

In addition to the uniqueness or lack thereof of the final symmetry, i.e. either  $D_{2h} \rightarrow C_{2h}$  or  $C_{2v} \rightarrow C_s$ . There is also the question of uniqueness of the  $n$ th iterated bond order matrix given that the final result is of a particular symmetry. To test this two arbitrary  $D_{2h}$  symmetry first order bond matrices were taken as starting points for the iterative procedure on pentalene and the final results were the same  $C_{2h}$  bond order matrices.

TABLE: 7.1

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION<sup>s</sup>

Molecule	Density Matrix			
	Bond	0	40	60
Pentalene $\delta = 0.40$	1-2	0.6540	0.6548	0.6550
	1-8	0.5179	0.5165	0.5162
	2-3	0.6540	0.6547	0.6544
	3-4	0.5179	0.5166	0.5168
	4-5	0.5179	0.5164	0.5162
	4-8	0.5393	0.5422	0.5422
	5-6	0.6540	0.6547	0.6550
	6-7	0.6540	0.6547	0.6544
	7-8	0.5179	0.5166	0.5168

TABLE: 7.1 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION<sup>s</sup>

Molecule	Density Matrix			
	Bond	0	40	60
Pentalene	1-2	0.6499	0.1647	0.1647
D <sub>2h</sub>	1-8	0.5243	0.9585	0.9585
	2-3	0.6499	0.9734	0.9734
	3-4	0.5243	0.1562	0.1562
$\delta = 0.80$	4-8	0.5309	0.1738	0.1738

<sup>s</sup> The calculations were carried out in single precision  
format in IBM 360/50K.

TABLE: 7.2

THE DENSITY MATRIX ELEMENTS AT SEVERAL STAGES OF ITERATION<sup>s</sup>

Molecule	Density Matrix					
	Bond	0	40	60	80	100
Pentalene $\delta = 0.40$	1-2	0.64988724	0.65472300	0.65472300	0.65472300	0.65472300
	1-8	0.52434547	0.51650640	0.51650640	0.51650640	0.51650640
	2-3	0.64988724	0.65472300	0.65472300	0.65472300	0.65472300
	3-4	0.52434547	0.51650640	0.51650640	0.51650640	0.51650640
	4-8	0.53088923	0.54218364	0.54218364	0.5421834	0.54218364
Pentalene $\delta = 0.60$	1-2	0.64988724	0.65880048	0.66027546	0.92192368	0.92196174
	1-8	0.52434547	0.50890409	0.50737301	0.24700069	0.24698299
	2-3	0.64988724	0.65880048	0.65732368	0.29076346	0.29065927
	3-4	0.52434547	0.50890409	0.51043705	0.87027650	0.87035872
	4-8	0.53088923	0.55438181	0.55437791	0.32566861	0.32552571

TABLE: 7.2 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL STAGES OF ITERATION<sup>s</sup>

Molecule	Density Matrix					
	Bond	0	40	60	80	100
Pentalene $\delta = 0.80$	1-2	0.64988724	0.89906921	0.97341777	0.97341777	0.97341777
	1-8	0.52434547	0.23837876	0.15623307	0.15623307	0.15623307
	2-3	0.64988724	0.36282220	0.16468847	0.16468847	0.16468847
	3-4	0.52434547	0.81459590	0.95854294	0.95854294	0.95854294
	4-8	0.53088923	0.42130409	0.17384755	0.17384755	0.17384755

<sup>s</sup> The calculations were carried out in double precision format in IBM 360/50K.

TABLE: 7.3

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0	40	60
Pentalene	1-2	0.7608	0.9024	0.9024
C <sub>2h</sub> $\delta = 0.40$	1-8	0.4159	0.2670	0.2670
	2-3	0.5322	0.3321	0.3321
	3-4	0.6316	0.8207	0.8207
	4-5	0.4159	0.2670	0.2670
	4-8	0.5248	0.4083	0.4083
	5-6	0.7608	0.9024	0.9024
	6-7	0.5322	0.3321	0.3321
	7-8	0.6316	0.8207	0.8207

TABLE: 7.3 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0	40	60
Pentalene $C_{2h}$ $\delta = 0.80$	1-2	0.7608	0.9930	0.9930
	1-8	0.4159	0.0811	0.0811
	2-3	0.5322	0.0850	0.0850
	3-4	0.6316	0.9790	0.9790
	4-5	0.4159	0.8110	0.8110
	4-8	0.5248	0.1676	0.1676
	5-6	0.7608	0.9930	0.9930
	6-7	0.5322	0.8504	0.8504
	7-8	0.6316	0.9790	0.9790
Pentalene $C_{2v}$ $\delta = 0.20$	1-2	0.6495	0.6511	0.6511
	1-8	0.5406	0.5417	0.5417
	7-8	0.4976	0.4870	0.4870
	6-7	0.6537	0.6572	0.6572
	4-8	0.5425	0.5496	0.5496

TABLE: 7.3 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0	40	60
Pentalene	1-2	0.6495	0.6530 <sup>†</sup>	0.6530
C <sub>2v</sub>	1-8	0.5406	0.5444	0.5443
δ = 0.40	7-8	0.4976	0.4694	0.4694
	6-7	0.6537	0.6626	0.6626
	4-8	0.5425	0.5607	0.5607
Pentalene	1-2	0.6495	0.3132 <sup>†</sup>	0.3116
C <sub>2v</sub>	1-8	0.5406	0.8738	0.8749
δ = 0.60	2-3	0.6495	0.9066	0.9074
	3-4	0.5406	0.2888	0.2879
	4-5	0.4976	0.8586	0.8601
	4-8	0.5425	0.3468	0.3446
	5-6	0.6537	0.2554	0.2535
	6-7	0.6537	0.9454	0.9459
	7-8	0.4976	0.1818	0.1822

<sup>†</sup> For δ = 0.40 and 0.60, the convergence rate is very slow.



TABLE: 7.3 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0(C <sub>2v</sub> )	40(C <sub>s</sub> )	60(C <sub>s</sub> )
Pentalene	1-2	0.6495	0.1758	0.1758
$\delta = 0.80$	1-8	0.5406	0.9638	0.9638
	2-3	0.6495	0.9680	0.9680
	3-4	0.5406	0.1814	0.1814
	4-5	0.4976	0.9604	0.9604
	4-8	0.5425	0.1873	0.1873
	5-6	0.6537	0.0972	0.0972
	6-7	0.6537	0.9916	0.9916
	7-8	0.4977	0.0807	0.0807

TABLE: 7.3 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0	40	60
Pentalene	1-2	0.7585	0.8969	0.8969
$C_s$	1-8	0.4260	0.2829	0.2829
$\delta = 0.40$	2-3	0.5343	0.3396	0.3396
	3-4	0.6374	0.8233	0.8233
	4-5	0.4002	0.2412	0.2412
	4-8	0.5311	0.4174	0.4174
	5-6	0.7657	0.9127	0.9127
	6-7	0.5303	0.3192	0.3192
	7-8	0.6211	0.8146	0.8146

TABLE: 7.3 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0	40	60
Pentalene $C_8$ $\delta = 0.80$	1-2	0.7585	0.9925	0.9925
	1-8	0.4260	0.0859	0.0859
	2-3	0.5343	0.0865	0.0865
	3-4	0.6374	0.9802	0.9802
	4-5	0.4002	0.0419	0.0419
	4-8	0.5311	0.1743	0.1743
	5-6	0.7657	0.9980	0.9980
	6-7	0.5303	0.4631	0.4631
	7-8	0.6211	0.9799	0.9799

TABLE: 7.4

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0	40	60
Azulene $\delta = 0.40$	1-2	0.6640	0.6660	0.6660
	1-10	0.5858	0.5926	0.5926
	2-3	0.6389	0.6382	0.6382
	8-9	0.6560	0.6555	0.6555
	9-10	0.5956	0.6052	0.6052
	6-10	0.4009	0.3647	0.3647
Azulene $\delta = 0.60$	1-2	0.6640	0.6658	0.6658
	1-10	0.5858	0.6006	0.6006
	2-3	0.6389	0.6383	0.6383
	8-9	0.6560	0.6542	0.6542
	9-10	0.5956	0.6147	0.6147
	6-10	0.4009	0.3259	0.3259

TABLE: 7.4 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0	40	100
Azulene $\delta = 0.80$	1-2	0.6640	0.6590	0.1040
	1-10	0.5858	0.6203	0.9496
	2-3	0.6389	0.6431	0.9641
	3-4	0.6389	0.6385	0.1878
	4-5	0.6640	0.6634	0.9658
	5-6	0.5858	0.6159	0.1847
	6-7	0.5956	0.6332	0.9498
	6-10	0.4009	0.2415	0.1742
	7-8	0.6560	0.6488	0.1939
	8-9	0.6560	0.6532	0.9644
	9-10	0.5950	0.6288	0.1855

TABLE: 7.4 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0	40	60
As-indacene $\delta = 0.50$	1-2	0.4947	0.3904	0.3904
	1-12	0.6757	0.7920	0.7920
	2-3	0.7905	0.8667	0.8667
	3-4	0.3884	0.3268	0.3268
	4-12	0.4641	0.3772	0.3772
	4-5	0.7016	0.7954	0.7954
	5-6	0.5034	0.4261	0.4261
	11-12	0.4160	0.3422	0.3422
As-indacene $\delta = 0.80$	1-2	0.4947	0.1837	0.1837
	1-12	0.6757	0.9516	0.9516
	2-3	0.7905	0.9678	0.9678
	3-4	0.3884	0.1750	0.1750
	4-12	0.4641	0.1790	0.1790
	4-5	0.7016	0.9508	0.9508
	5-6	0.5034	0.1945	0.1945
	11-12	0.4160	0.1762	0.1762

TABLE: 7.4 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0	40	60
Naphthalene	1-2	0.7246	0.7493	0.7493
$D_{2h}$	1-9	0.5547	0.5378	0.5378
$\delta = 0.40$	2-3	0.6032	0.5721	0.5721
	9-10	0.5182	0.5448	0.5448
Naphthalene	1-2	0.7246	0.7828	0.7828
$D_{2h}$	1-9	0.5547	0.5083	0.5083
$\delta = 0.60$	2-3	0.6032	0.5287	0.5287
	9-10	0.5182	0.5927	0.5927
Naphthalene	1-2	0.7246	0.9857	0.9857
$D_{2h}$	1-9	0.5547	0.1261	0.1261
$\delta = 0.90$	2-3	0.6032	0.1253	0.1253
	9-10	0.5182	0.9715	0.9715

TABLE: 7.4 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0	40	60
Heptalene  $\delta = 0.40$	1-2	0.6722	0.6840	0.6840
	1-11	0.5357	0.5265	0.5265
	2-3	0.6187	0.6133	0.6133
	3-4	0.6187	0.6133	0.6133
	4-5	0.6722	0.6840	0.6840
	5-12	0.5357	0.5265	0.5265
	11-12	0.5024	0.5120	0.5120
Heptalene  $\delta = 0.70$	1-2	0.6722	0.9381	0.9381
	1-11	0.5357	0.2437	0.2437
	2-3	0.6187	0.2533	0.2533
	3-4	0.6187	0.9322	0.9322
	4-5	0.6722	0.2685	0.2685
	5-12	0.5357	0.9046	0.9046
	11-12	0.5024	0.2479	0.2479



TABLE: 7.4 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0(D <sub>2h</sub> )	40(C <sub>2h</sub> )	60(C <sub>2h</sub> )
Heptalene $\delta = 0.90$	1-2	0.6722	0.9914	0.9914
	1-11	0.5357	0.0925	0.0925
	2-3	0.6187	0.0929	0.0929
	3-4	0.6187	0.9913	0.9913
	4-5	0.6722	0.0939	0.0939
	5-12	0.5357	0.9871	0.9871
	11-12	0.5024	0.0922	0.0922
Molecule	Density Matrix <sup>†</sup>			
	Bond	0	40	60
Dibenz- pentalene $\delta = 0.50$	1-2	0.6115	0.5677	0.5677
	1-16	0.6896	0.7191	0.7191
	2-3	0.7083	0.7479	0.7479
	3-4	0.5520	0.5172	0.5172
	4-5	0.5727	0.5968	0.5968
	4-15	0.4852	0.4889	0.4889
	5-6	0.5405	0.5310	0.5310
	6-14	0.5281	0.5434	0.5434
	14-15	0.4821	0.4752	0.4751
	15-16	0.5949	0.5810	0.5810

<sup>†</sup> The convergence rate is slow.

TABLE: 7.4 cont'd

THE DENSITY MATRIX ELEMENTS AT SEVERAL  
STAGES OF ITERATION

Molecule	Density Matrix			
	Bond	0	40	60
Dibenz- pentalene  $\delta = 0.80$	1-2	0.6115	0.1826	0.1826
	1-16	0.6896	0.9667	0.9667
	2-3	0.7083	0.9682	0.9681
	3-4	0.5520	0.1790	0.1790
	4-5	0.5727	0.9559	0.9559
	4-15	0.4852	0.1661	0.1661
	5-6	0.5405	0.1627	0.1627
	6-7	0.5405	0.9545	0.9546
	6-14	0.5281	0.1817	0.1817
	7-8	0.5726	0.1713	0.1711
	8-9	0.5520	0.3615	0.3578
	8-13	0.4852	0.8676	0.8696
	9-10	0.7083	0.8954	0.8973
	10-11	0.6115	0.3596	0.3560
	11-12	0.6896	0.8953	0.8972
	12-13	0.5949	0.3618	0.3582
	13-14	0.4821	0.1680	0.1678
	14-15	0.4821	0.9380	0.9381
	15-16	0.5949	0.1865	0.1864

TABLE: 7.4

THE DENSITY MATRIX ELEMENTS AT SEVERAL STAGES OF ITERATION FOR MODEL NON-ALTERNANTS

Molecule	Bond	Density Matrix, $\delta = 0.40$			Density Matrix, $\delta = 0.80$		
		0	40	60	0	40	60
Model I	1-2	0.4056	0.3483	0.3483	0.4056	0.1751	0.1751
	1-12	0.8304	0.8753	0.8753	0.8304	0.9691	0.9691
	2-3	0.6523	0.6880	0.6880	0.6523	0.8936	0.8937
	2-13	0.5160	0.5124	0.5124	0.5160	0.3263	0.3262
	3-4	0.6103	0.5937	0.5937	0.6103	0.3395	0.3395
	13-14	0.5307	0.5522	0.5522	0.5307	0.8259	0.8259
Model II	1-2	0.5812	0.6096	0.6096	0.5812	0.9434	0.9434
	1-13	0.6829	0.6642	0.6642	0.6829	0.2118	0.2118
	2-3	0.5247	0.4923	0.4923	0.5247	0.1859	0.1859
	2-14	0.4769	0.4624	0.4624	0.4769	0.1903	0.1903
	3-4	0.7185	0.7603	0.7603	0.7185	0.9655	0.9655
	4-5	0.5684	0.5187	0.5187	0.5684	0.1881	0.1881
	5-6	0.7221	0.7623	0.7623	0.7221	0.9644	0.9644
	6-7	0.5168	0.4881	0.4881	0.5168	0.1916	0.1916
	7-14	0.5555	0.5919	0.5919	0.5555	0.9291	0.9291

TABLE: 7.5

THE LOWEST-LYING EIGENVALUE (IN ELECTRON VOLTS)  $\lambda_1$ , OF THE CHARACTERISTIC-VALUE  
PROBLEM, CALCULATED USING THE "THEORETICAL" PARAMETRIZATION AND "PPP" PARAMETRIZATION

System	"Theoretical" Parametrization <sup>§</sup>				"PPP" Parametrization <sup>†</sup>			
	$(0)\bar{H}_{rs}^x$	$\lambda$ (a)	$(0)\bar{H}_{rs}^x$	$\lambda$ (b)	$(0)\bar{H}_{rs}^x$	$\lambda$ (a)	$(0)\bar{H}_{rs}^x$	$\lambda$ (b)
Pentalene	0.1	-1.033	0.1	-1.598	0.1	-0.443	0.1	-0.688
	0.4	-0.416	0.3	-1.066	0.4	-0.063	0.4	-0.224
	0.7	0.137	0.7	-0.176	0.7	0.281	0.7	0.163
	1.0	0.675	0.9	0.618	1.0	0.619	1.0	0.527
	-		1.3	0.999	1.3	0.956	1.3	0.881
	-		1.5	1.373	1.6	1.293	-	1.228

<sup>§</sup> The value of  $\bar{H}_{rs}$  is -3.716 e.v.

<sup>†</sup> The value of  $\bar{H}_{rs}$  is -2.39 e.v.

TABLE: 7.6

THE LOWEST-LYING EIGENVALUE (IN ELECTRON VOLTS)  $\lambda_1$ , OF THE CHARACTERISTIC-VALUE PROBLEM, CALCULATED USING THE "THEORETICAL" PARAMETRIZATION AND "PPP" PARAMETRIZATION

System	"Theoretical" Parametrization <sup>§</sup>				"PPP" Parametrization <sup>†</sup>			
	$(0)\bar{H}_{rs}^x$	$\lambda$ (a)	$(0)\bar{H}_{rs}^x$	$\lambda$ (b)	$(0)\bar{H}_{rs}^x$	$\lambda$ (a)	$(0)\bar{H}_{rs}^x$	$\lambda$ (b)
Heptalene	0.1	-0.386	0.1	-1.153	0.1	-0.104	0.1	-0.475
	0.4	-0.065	0.4	-0.631	0.4	0.105	0.4	-0.174
	0.7	0.260	0.7	-0.177	0.7	0.297	0.7	0.086
	1.0	0.592	1.0	0.239	1.0	0.500	1.0	0.331
	1.3	0.929	1.3	0.633	1.3	0.709	1.3	0.569
	1.6	1.268	1.6	1.014	1.6	-	1.6	0.802

<sup>§</sup> The value of  $\bar{H}_{rs}$  is -3.716 e.v.

<sup>†</sup> The value of  $\bar{H}_{rs}$  is -2.39 e.v..

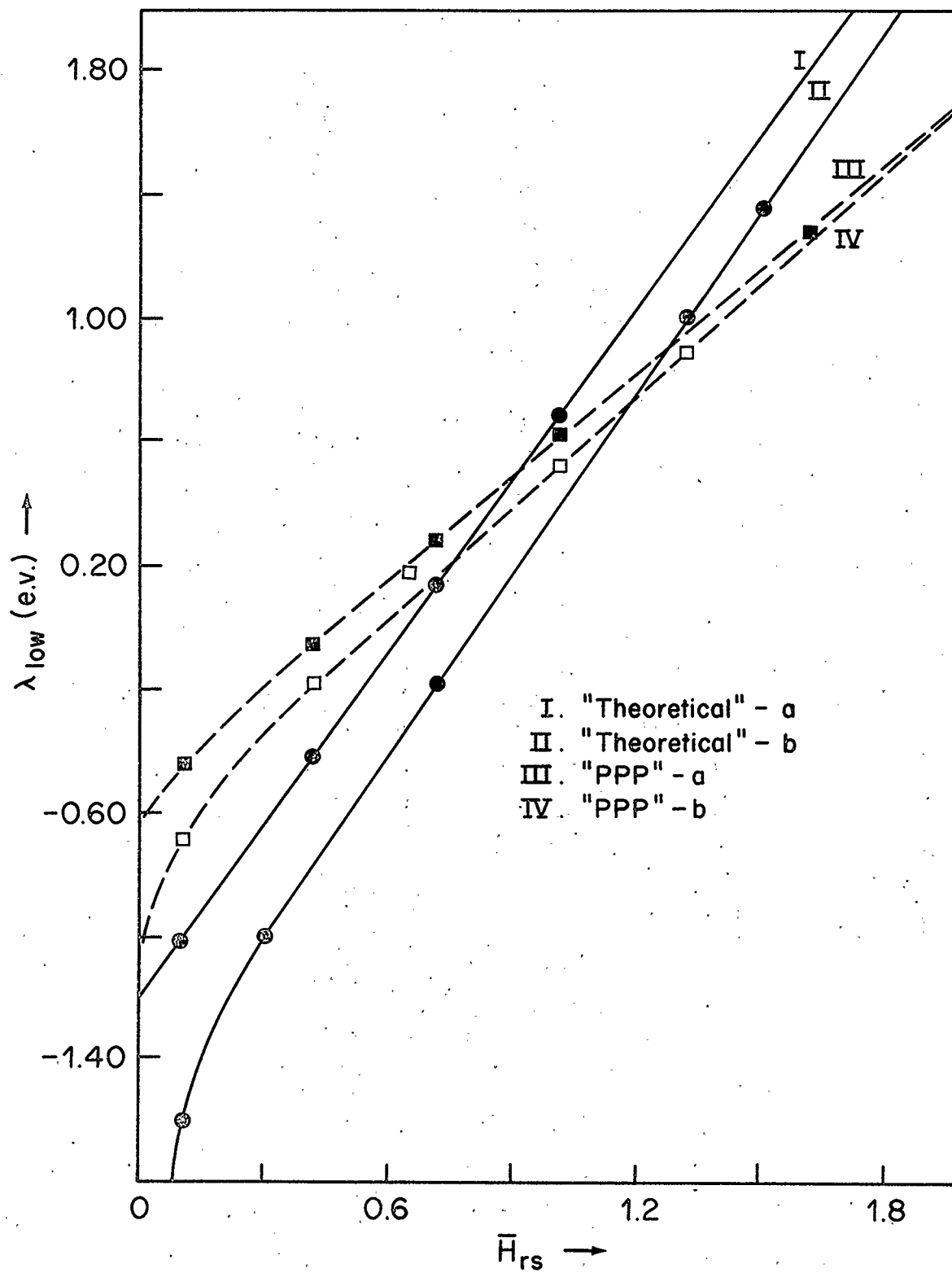


Figure 7.1: Plot of the lowest eigenvalue,  $\lambda$ , (e.v.), against the core integral,  $\bar{H}_{rs}$ , for pentalene.

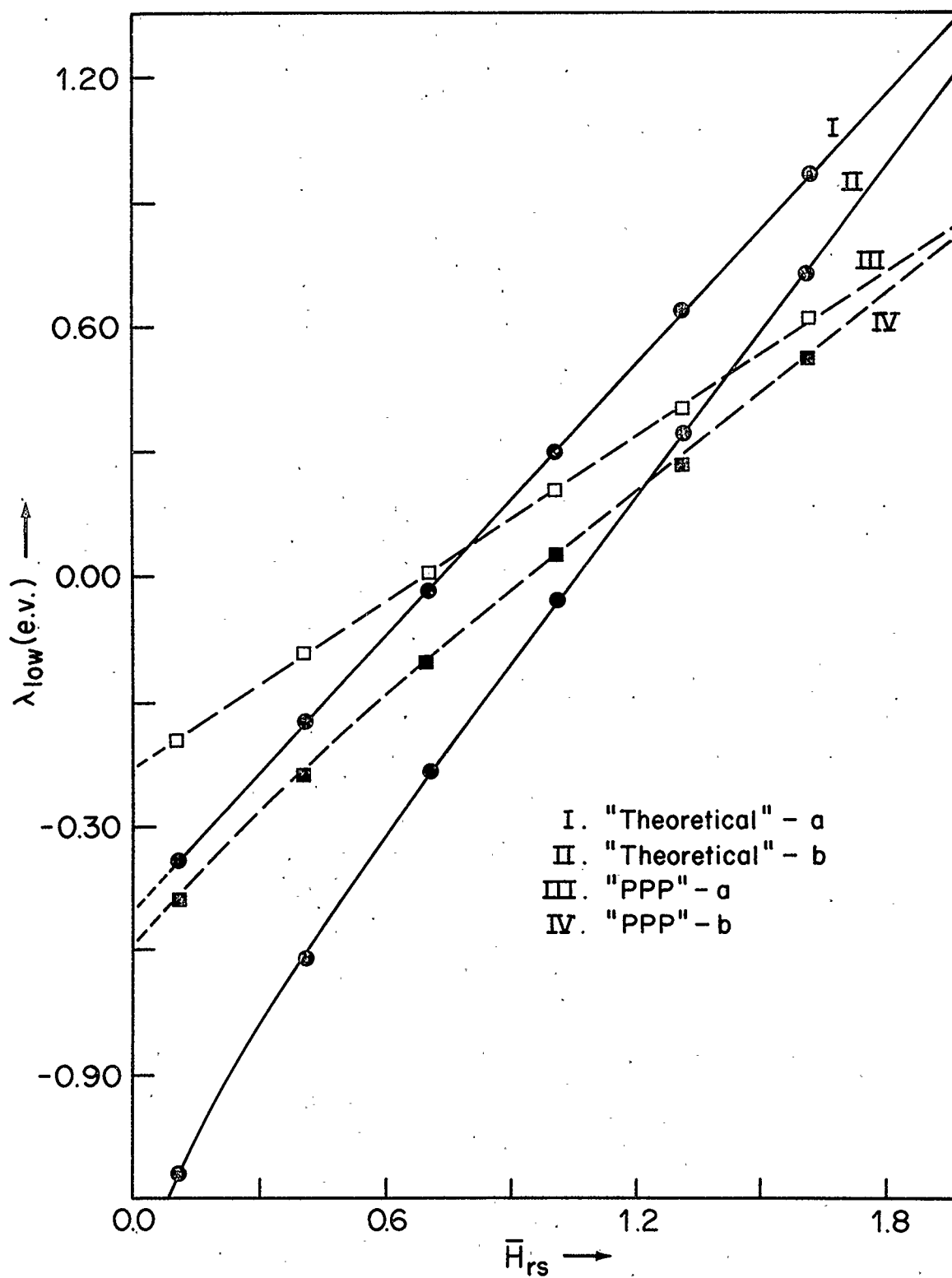


Figure 7.2: Plot of the lowest eigenvalue,  $\lambda$ , (e.v.), against the core integral,  $\bar{H}_{rs}$ , for heptalene.

## CHAPTER 8

### CONCLUDING REMARKS

#### 8.10: SUMMARY

Although we have restricted ourselves to first order perturbations in the analytical study detailed in this thesis, we have obtained a closed form expression for the  $n^{\text{th}}$  iterated bond order matrix. Within this context we have been able to examine both the criteria for convergence and in an illustrative example the contributions to the final bond order corrections. The analysis could, of course, be extended to include second order terms (but the complexity of the expression does not auger well for a useful analysis). We have been able to extend the work to infinite systems and for these cases to establish not only the convergent form of  $(n)_r^P$  but also the rate of convergence and the oscillations from iteration to iteration. Using parametrizations obtained on a statistical basis but in reasonable agreement with those obtained on the basis of specific models, the application of the method to several classes of pi-electron systems yields results in good agreement with experiment for a wide variety of systems.

Finally, we have found that for certain molecules, the initial symmetry is lost after a number of iterations under the conditions similar to those known to lead to "instability" in



other systems. A more formal analysis of the "instability" in terms of the sign of the second variation of the energy functional yields an instability for essentially the same conditions, namely a relatively large ratio of the repulsion to the core matrix elements.

#### 8.20: FURTHER WORK

Notwithstanding the apparent relation between  $\delta$  and the largest eigenvalue of the polarizability matrix and the onset of loss of symmetry, this is still an area of some concern. In particular, an attempt to establish non-analyticity for the "critical" range of  $\delta$  would be useful in understanding just how the symmetry is lost.

Further, in view of the apparent singlet "instability" of the Hartree-Fock solution of pentalene ( $D_{2h}$ ) and heptalene ( $D_{2h}$ ) it is perhaps useful to investigate other non-alternant hydrocarbons which have not been subjected to any "stability" study.

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APPENDIX: 1

MATRIX ELEMENTS

Following Ito and I'Haya<sup>59</sup> and Cizek,<sup>60</sup> the matrix elements of **A** and **B** are given below:

DIAGONAL ELEMENTS OF **A** :

$$\begin{aligned}
 \left\langle \begin{smallmatrix} j \\ i \end{smallmatrix} \middle| \hat{Q} \middle| \begin{smallmatrix} j \\ i \end{smallmatrix} \right\rangle &= 2 \left\langle ji | \hat{v} | ij \right\rangle - \left\langle ji | \hat{v} | ji \right\rangle \\
 &+ \left\langle i | i \right\rangle \left\langle j | \hat{h} | j \right\rangle - \left\langle j | j \right\rangle \left\langle i | \hat{h} | i \right\rangle \\
 &+ \sum_{a'}^{\text{occ}} \left( 2 \left\langle ja' | \hat{v} | ja' \right\rangle - \left\langle ja' | \hat{v} | a'j \right\rangle \right) \\
 &- \sum_{a'}^{\text{occ}} \left( 2 \left\langle ia' | \hat{v} | ia' \right\rangle - \left\langle ia' | \hat{v} | a'i \right\rangle \right)
 \end{aligned}$$

OFF-DIAGONAL ELEMENTS OF **A** :

$$\begin{aligned}
 \left\langle \begin{smallmatrix} j \\ i \end{smallmatrix} \middle| \hat{Q} \middle| \begin{smallmatrix} j \\ k \end{smallmatrix} \right\rangle &= 2 \left\langle jk | \hat{v} | ij \right\rangle - \left\langle jk | \hat{v} | ji \right\rangle \\
 &- \left\langle j | j \right\rangle \left\langle i | \hat{h} | k \right\rangle \\
 &- \sum_{a'}^{\text{occ}} \left( 2 \left\langle ia' | \hat{v} | ka' \right\rangle \right) \\
 &- \left\langle ia' | \hat{v} | a'k \right\rangle
 \end{aligned}$$



$$\begin{aligned}
 \left\langle \begin{smallmatrix} j \\ i \end{smallmatrix} \middle| \hat{Q} \middle| \begin{smallmatrix} \ell \\ i \end{smallmatrix} \right\rangle &= 2 \left\langle ji | \hat{v} | i\ell \right\rangle - ji | \hat{v} | \ell i \\
 &+ \left\langle i | i \right\rangle \left\langle j | \hat{h} | \ell \right\rangle \\
 &+ \sum_{a'}^{\text{occ}} \left( 2 \left\langle ja' | \hat{v} | \ell a' \right\rangle \right. \\
 &\left. - \left\langle ja' | \hat{v} | a' \ell \right\rangle \right)
 \end{aligned}$$

$$\left\langle \begin{smallmatrix} j \\ i \end{smallmatrix} \middle| Q \middle| \begin{smallmatrix} \ell \\ k \end{smallmatrix} \right\rangle = 2 \left\langle jk | \hat{v} | i\ell \right\rangle - \left\langle jk | \hat{v} | \ell i \right\rangle$$

DIAGONAL ELEMENTS OF **B** :

$$\left\langle \begin{smallmatrix} j & j \\ i & i \end{smallmatrix} \middle| \hat{Q} \middle| \Phi_0 \right\rangle = \left\langle jj | \hat{v} | ii \right\rangle$$

OFF-DIAGONAL ELEMENTS OF **B** :

$$\left\langle \begin{smallmatrix} j & j \\ i & k \end{smallmatrix} \middle| \hat{Q} \middle| \Phi_0 \right\rangle = -\sqrt{2} \left\langle jj | \hat{v} | ik \right\rangle$$

$$\left\langle \begin{smallmatrix} j & \ell \\ i & i \end{smallmatrix} \middle| \hat{Q} \right| \Phi_0 \rangle = \sqrt{2} \langle j\ell | \hat{v} | ii \rangle$$

$$\left\langle \begin{smallmatrix} j & \ell \\ i & k \end{smallmatrix} \middle| \hat{Q} \right| \Phi_0 \rangle = \langle j\ell | \hat{v} | ki \rangle - \langle j\ell | \hat{v} | ik \rangle$$