SOME PROBLEMS IN THE COMPUTATION OF ELECTRONIC WAVE FUNCTIONS

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ABSTRACT

Four problems in the application of electronic digital computers to the theoretical treatment of π-electron systems in molecules are treated.

A General Introduction outlines the basic assumptions which underlie the work and explains the method of presentation, including the methods used to describe computer programmes. Print-outs of some of the programmes used are provided in appendices for reference.

The four problems are presented in a chapter each and are:

I. Programmes for the computation of Hückel Molecular Orbitals and derived quantities.

The development of programmes for calculation, in the Hückel approximation, of molecular orbital energies, coefficients, π-electron charges, bond orders, free valences and the various mutual polarizability coefficients is described. These were developed in connection with the task of producing a book* of tables of these quantities by photolithography from computer output. Points considered include the design of the layout of the results, the ways of utilizing molecular symmetry both to reduce the size of tables and to shorten the calculation, the details of the presentation of data to the programme to define the molecule and calculations required, the details of the coding of the programme and the possibility of running it on other computers than Mercury.

Some calculations done with the programmes on some molecules recently synthesized are also reported, and a brief

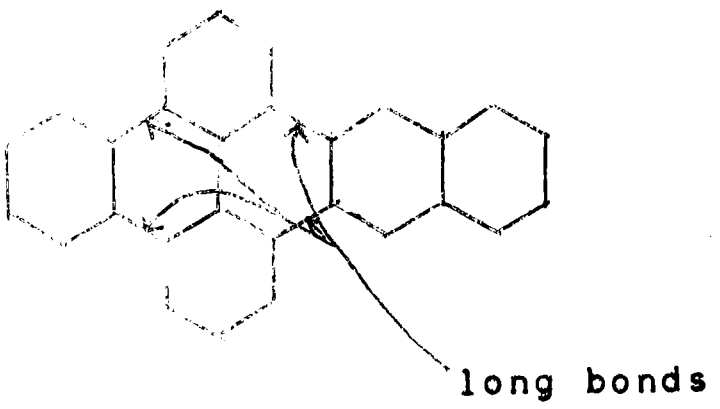
*'Dictionary of π-electron calculations', C.A. Coulson and A. Streitwieser, Jr. Pergamon (in Press).

study is made of the effect of varying the Coulomb terms and resonance integrals in the pyridine-like and pyrrole-like systems.

II. A Self-consistent Hückel Molecular Orbital Method. Programmes are described which are an extension of those described in chapter I. These may be used to calculate molecular orbitals which are self-consistent insofar as, given semi-empirical relations between charges and bond orders on the one hand and Coulomb terms and resonance integrals on the other, the set of charges and bond orders calculated from a solution of the secular equations is the same as that assumed in setting them up. The method of calculation is by an iterative process and a method of speeding convergence by taking a suitable mean from three iterations is developed. The application of the programme to non-alternant hydrocarbons is discussed and it is shown that the method gives improved predictions of certain experimental quantities compared with the simple Hückel method. The application of the method to alternant hydrocarbons where only the bonds are not self-consistent is considered and calculations on some cyclobutadiene derivatives are discussed. The possibility of using the programmes for heterosystems is mentioned and the trouble of the difficulty of making suitable parameter choices for these molecules is pointed out.

III. The Ultraviolet spectra of benzologues of pyrene. The electronic spectra of a large number of molecules derived from pyrene by annelation of benzene rings in various directions have been reported by Clar. The lowest such

transition is known to be correlated with the energy of the top orbital in the Hückel approximation, and the programmes of Chapter I are used to calculate Hückel orbitals for these molecules. It is observed that the molecules where annelation is linear and is such that they may be considered as polyacenes with benzene rings fused at both sides at one point in the chain have bond orders which indicate long bonds joining the central diphenyl group to the 'side chains' (see Figure)



Consequently a method due to Longuet-Higgins and Murrell is extended to consider these molecules as built up from several fragments joined by these long bonds, with the intention of using known spectra of the fragments to predict the spectra of the complete molecules. Programmes are described which take in data concerning the fragments and their orbitals and the configurational wave functions to be considered and solve the appropriate configuration interaction problem. The choice of suitable experimental data is discussed and the results of calculations on these molecules are reported. Although some qualitative features of the observed spectra are reproduced the method is found not to be very good quantitatively. The results of other calculations on these molecules are mentioned and compared with the predictions of the Hückel method. It is concluded that no significant improvement on the latter can be expected by any simple method.

IV. The effects on π-electron energy of the formation of a vacancy in a graphite layer.

Programmes are described which calculate the total π-energy of large fragments of the plane hexagonal array of carbon atoms which constitute a layer of the graphite crystal. The effect of removing from the layer one, two, or four atoms at a place chosen as origin of coordinates is calculated. By choosing fragments with the maximum symmetry (D_{3h}) considerable reductions in the size of matrices which need to be handled may be made. The use of group theory to effect these reductions is fully described. The results of the calculations are presented and certain irregularities in the numerical answers are correlated with the possibility or otherwise of drawing Kekulé structures for certain fragments with and without the central atoms. In order to obtain a series of fragments where the required energy difference tends to a limit in a reasonably smooth manner, fragments with D_{2h} symmetry are considered. The energy required to remove one, two or four atoms from the conjugated system is found to be 2.75 ± 0.02, 4.52 ± 0.01, 8.65 ± 0.04, in units of the standard resonance integral β, respectively. A brief discussion is given of the relation of these quantities to others involved in the formation of vacancies. It is concluded that it is probably unfavourable for the neighbour atoms to a single vacancy to change hybridization from $sp^2\pi$ to s^2p^2 and so leave the conjugated system. It is also concluded that it is energetically favourable for two isolated vacancies to come together and form a divacancy.

GENERAL INTRODUCTION

In the past 15 years the electronic digital computer has advanced from the stage of an electronic engineer's toy to being considered a sine qua non for the majority of research, both practical and theoretical, in the physical, and now increasingly in the biological and social, sciences. Many mathematical theories of the physical world may be worked out very fully using the symbolic language of algebra, but few can be compared with observation and experiment without considerable numerical computation. This numerical computation, being something which may be well-defined in terms of logic and arithmetic, is easily carried out by a machine which is designed to obey the elementary rules of logic and arithmetic from which all calculations may be considered to be built. Nowadays it is being increasingly realized that it is not only the conventional numerical analysis which is susceptible to automatic treatment. Many other processes, both clerical and mathematical, are capable of description in logical terms so that they may be carried out by a computer.

Although the four problems considered in the present thesis are essentially numerical, every opportunity has been taken to use the computer for as much of the problem as possible, because of its much greater reliability than human beings.

The field of theoretical chemistry is a very rich one for computational problems, and several groups of workers, especially in the United States, are concerned solely with such computations. The methods applicable to chemical systems may first be divided into two groups; the ab-initio calculations where an attempt is made to solve Schrödinger's

equation to a very high degree of accuracy for atomic and molecular systems, and the semi-empirical calculations where one does not attempt a complete prediction of numerical quantities concerned with molecules but is satisfied with correlations and systematizations of observed and calculated numbers. The former type of calculations when applied to molecules of any size involve such a large amount of computation and the storage of such a large amount of intermediate results that they are only economic in terms of time and money when carried out on the largest and fastest computer available. The magnitude of many of these problems often makes it necessary to split them into several stages and distribute the effort among a team of people if results are to be obtained in a reasonable time. They are thus not easily compatible with the British system of higher degrees whereby each research student must at least pretend to have worked as an individual. The relatively small size of the Mercury computer available at Oxford was another factor affecting the choice of problems.

The problems of the present thesis are thus chosen from the second type of calculation, where the mathematics is made very much simpler by means of assumptions and approximations many of which are only justified a posteriori by the fact that the theory works. The four problems considered here arose independently but share a common feature in that they are concerned with π-electrons. These are the electrons concerned in the <u>double-bonds</u> familiar to organic chemists. The approximations and assumptions inherent in all the present work, include the following:

(a) The Born-Oppenheimer or fixed nucleus approximation. This enables us to consider the motion of the electrons

separately from that of the nuclei, which, being very much heavier, move very much more slowly.

(b) The orbital approximation.

The Schrödinger equation for the motion of electrons in a molecule may be written:

$$\mathcal{H}_e(\underline{r}/\underline{R}) \quad \Psi_e(\underline{r}/\underline{R}) = E(R) \; \Psi_e(\underline{r}/\underline{R}) \qquad (1)$$

The electronic Hamiltonian operator $\mathcal{H}_e$ is a function of the positions of all the electrons (collectively represented by $\underline{r}$) for any positions of the nuclei ($\underline{R}$). The electronic wave function Ψ_e is also such a function. The energy E is the <u>eigenvalue</u> of the operator $\mathcal{H}$ corresponding to the <u>eigenfunction</u> Ψ. <u>The total electronic wave function</u> Ψ may be approximated by a product (or a linear combination of products) of <u>one-electron wave functions</u> or <u>orbitals</u> ψ_j.

In using the orbital approximation we are assuming that the motion of each electron is independent of that of all the others, or at the best, that the effect of the others may be represented by some smoothed-out field the interaction with which is represented by a potential energy term in the one electron Hamiltonian $\mathcal{H}_j$. Each orbital may be assumed to satisfy an equation of the form:

$$\mathcal{H}_j \; \psi_j = \epsilon_j \; \psi_j \qquad (2)$$

where the ϵ_j are one-electron or orbital energies.

(c) The LCAO-MO approximation.

When considering molecules one may concentrate on the chemical bonds, considering only the interactions between the electrons of complete atoms. This is the <u>valence bond</u> method. Alternatively we may consider the electrons to be all moving relatively independently in the field of all the nuclei; each electron may be considered to inhabit a <u>molecular orbital</u>. In order to carry out calculations on molecular orbitals, it is necessary to give them some sort

of mathematical form. A useful approximation is the <u>linear combination of atomic orbitals</u> method (LCAO) which arises as follows: when in the neighbourhood of one nucleus of the molecule any one electron is subjected to forces similar to those it would experience if it were in an atom containing that nucleus. Its wave function would thus be expected to resemble an <u>atomic orbital</u> for that atom. As this will hold for all the electrons when near all the nuclei in the molecule, each electron may be considered to inhabit a molecular orbital which is expressed as a linear combination of several atomic orbitals

$$\psi_j = \sum_r c_{rj} \phi_r \qquad (3)$$

It may be shown that only atomic orbitals with the same symmetry properties may be combined in such LCAO molecular orbitals. It is further necessary if all the c_{rj} are to be of comparable magnitude that the interacting atomic orbitals should have energies of similar magnitude and that their charge clouds should overlap to an appreciable extent. It thus appears that the inner shell electrons of the atoms will occupy molecular orbitals which approximate very closely to atomic orbitals, but that the outer, bonding, electrons may be said to inhabit truly molecular orbitals which extend all over the molecule.

(d) the π-electron approximation.

A very important group of molecules are the planar molecules typified by those known to organic chemists as aromati hydrocarbons and conjugated hydrocarbons. The valence shell of the carbon atom contains four electrons and in these molecules each atom forms three equivalent σ-bonds pointing at directions 120° from each other and has also a single π-electron which interacts with others to form a <u>delocalized</u>

<u>π-bond</u> (σ-electrons are cylindrically symmetric about a bond, π-electrons have wave functions anti-symmetric with respect to a plane passing through the bond).

Most of the properties of aromatic hydrocarbons and molecules analogous to them containing atoms other than carbon may be shown to be concerned solely with the π-electrons, which because of their symmetry do not interact with the σ-electrons and because of their similar energy and considerable overlap at usual C-C bond distances interact extensively among themselves. It is for these reasons that the greater part of the theoretical study of these molecules is concerned solely with these electrons.

Further discussion of the principles, the approximations and the derivation of the equations of LCAO-MO theory may be found in any of the standard text-books and is omitted here. We will now describe the four problems treated in the present thesis.

(i) The computation of Hückel molecular orbitals and derived quantities.

The simplest version of LCAO-MO theory applicable to π-electron systems is that due to Hückel. No explicit form of the one electron Hamiltonian need be defined and all quantities calculated from the theory are given in terms of the LCAO coefficients c_{rj} and the orbital energies ϵ_j. A very large number of calculations have been done by this method both on desk calculating machines and using computers. The present work is only original insofar as some molecules are treated which have not been treated before and, more important, that the programmes described here have been designed to accept the minimum of data defining the molecule and the calculation required and to

produce from these data a tabular output suitable for direct reproduction for publication. The programmes have been written in the Mercury Autocode language and so may be used on computers other than Mercury if suitable compilers are available.

(ii) A self-consistent Hückel molecular orbital method. Many π-electron systems are not adequately treated by the simple Hückel method, one defect of which is to start with assumptions concerning the equivalence of all atoms and of all bonds, but to derive results inconsistent with this. By finding relations between the output quantities and the input one may derive an iterative scheme leading to self-consistent results. Similar calculations to the present ones have been done before on different sets of molecules.

(iii) The ultraviolet spectra of benzologues of pyrene. The full treatment of ultraviolet spectra of aromatic hydrocarbons usually involves considerable calculations of interactions between configurations etc. Comprehensive programmes for these sorts of calculation have been written and used by Koutecký and his coworkers at Prague and by Ruedenberg and coworkers at Baltimore. The present work is concerned with the use of the Hückel method to predict approximate absorption frequencies for a series of hydrocarbons synthesized by Clar at Glasgow. One series of these molecules shows properties which makes it interesting to consider them as built up from fragments and a method of estimating transition energies of the molecules from the known spectra of the fragments is developed.

(iv) The effects on π-electron energy of the formation of vacancies in a graphite layer.

Graphite is the largest aromatic molecule conceivable. The crystal consist of layers of carbon atoms in a hexagonal array, and the electrical conductivity and other properties may be associated with the π-electrons which are considered to occupy practically infinite delocalized bonds. For a perfect crystal it is normal to treat the problem by the usual solid-state methods with periodic wave functions. The present problem, however, is concerned with the energy required to remove one or a few atoms, with their π-electrons, from the layer. In order to consider these it is necessary to consider finite fragments of the layer which may be treated by the Hückel method.

The Programmes

The computer at Oxford is a Ferranti Mercury, and the programmes described in this thesis were written specifically for this machine, although, as already mentioned, programmes written in the Autocode language may be accepted by other machines. The description of programmes in the thesis is on 3 different levels: A verbal description of the structure and properties of the programme; Flow Charts giving the main logical structure of the programme; and complete teleprinter print-outs, annotated with arrows to indicate the action of conditional and unconditional JUMP instructions and with brief verbal explanations of the computation. The print-outs which are only given for the programmes of chapter I and for one of those of chapter III are put in appendices as they do not form part of the logical development of the thesis.

A knowledge of certain features of the computer (the two-level store, the nature of the Autocode language, the addressing system and breakdown of a 40-bit word, etc.) is assumed. Certain conventions that have been used in representing the computer character set on a typewriter will be mentioned to avoid confusion:

(i) The letter O will be underlined to distinguish it from the digit 0.

(ii) The character alternatively known as 'π' or '$\not{\pi}$' will be represented by '$\not{\pi}$' as it is in all teleprinter output included in the thesis.

(iii) The character printed by the teleprinter as x (small x) will be represented by 'Ø'.

(iv) The prime (') will be represented by 'n' as on the teleprinter.

(v) O will be used to represent 'nought' except in such symbols as 'Eo' where a small 'o' seems more appropriate.

(vi) Capital letters will always be used when referring to Autocode variables.

All teleprinter print-out included in the thesis is original (i.e. was produced from punched tape). Unfortunately the margin is too small for these pages to be bound at the left. It is hoped that having them bound on the right will not cause too much difficulty in reading. In certain places it is felt that having matter on facing pages improves the intelligibility.

Mathematical and Chemical Notation and abbreviations

It is hoped that all notation not explained on introduction is either self-explanatory or sufficiently standard not to require explanation. The only completely novel symbols used are the affixes [illegible] which are introduced in section 3 of Chapter III.

The abbreviation 'no.' is only used for 'number' in the sense of 'code no.' or 'ordinal no.', never in the sense of 'quantity'. This distinction has been found useful to make clear the meaning of certain sentences. The converse does not hold in that the word 'number' may be used meaning a code number or ordinal number, etc.

Notation in flow charts: These charts which describe the action of computer programmes consist of four types of symbols: 'action blocks' which are rectangular and describe in imperative mood the action of a section of programme; 'decision blocks' which are diamond shaped, and usually contain a condition which may be true or false; 'lines' which indicate the sequence in which actions and decisions are taken. 'Action blocks' have one or more 'input' lines but only one 'output' line. Decision blocks have one or more 'input' and two 'outputs'. The outputs are labelled YES and NO and are followed according to the truth or falsity of the condition respectively. Finally there are 'labels' which are numbers followed by a ')' which correspond exactly to the labels in the programme itself and so should be of use in tracing the correspondence between the flow-chart and the programme.

Numbering of Chapters, Sections, Equations, Figures and Tables

Chapters: Large Roman numerals

Sections: Each chapter is divided into sections numbered with 'Arabic' numerals. Some sections are subdivided in a decimal notation.

Tables and Flow Charts: These are both numbered serially throughout each chapter

Equations: These are numbered serially throughout each section

Figures: These are numbered according to the section and sub-sections. Succeeding figures after the first in any one subsection are given letters of the alphabet.

Acknowledgements

Many people have helped with the work described in this thesis at various stages. Foremost among these is my Supervisor, Professor C. A. Coulson, F.R.S., who suggested the four problems and has helped me with them from start to finish. Secondly Dr. J. S. Rollett who has given me advice on programming and has helped to elucidate the computer's logical behaviour in reply to my illogical blunders. I would like also to thank the computer operators, Miss C. Bubb, Mrs. E. Chin, Mrs. A. Fluendy, Miss R. Miles and Miss D. Willcox who have tested the programmes so often for me; and the other members of the staff of Oxford University Computing Laboratory, who together with the regular visitors from departments all over the university and beyond must surely make up one of the most friendly and most useful groups of informed people on all aspects of computing to be found anywhere. I must further express my indebtedness to the other theoretical chemists in Oxford especially Mr. K. K. Banerjee, Mr. R. J. S. Crossley, Mr. D. S. Eisenberg, Mr. C. W. Haigh, Mr. D. A. Hutchinson and Mr. C. S. Sharma of the

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CHAPTER I

PROGRAMMES FOR COMPUTATION OF HUCKEL MOLECULAR ORBITALS AND DERIVED QUANTITIES.

1. The Huckel molecular orbital method.

This method, introduced by Hückel (1931), will be referred to as the HMO method. It is the simplest form of the LCAO (Linear combinations of atomic orbitals) method for calculating one-electron wave functions (molecular orbitals) for the π-electrons in planar aromatic and other conjugated hydrocarbons (and heteromolecules derived from them by replacement of certain carbon atoms by other atoms). For a bibliography of the method see e.g. Streitwieser (1961).

Each molecular orbital j is expressed as a linear combination of atomic orbitals thus:

$$\psi_j = \sum_{r=1}^{n} c_{rj}\phi_r = \underline{c}_j^{\dagger}\underline{\phi} \qquad (1.1)$$

$\underline{c}_j$ is a column vector with elements c_{rj}(r=1...n), $\underline{c}_j^{\dagger}$ is its transpose and $\underline{\phi}$ is a column vector with elements ϕ_r, where the ϕ_r are atomic orbitals (usually 2pπ orbitals).

The energy of an electron is represented by an effective one-electron Hamiltonian operator $\mathcal{H}$, the exact form of which need not be specified. The matrix elements of $\mathcal{H}$ in the basis $\underline{\phi}$ are defined thus:

$$\mathcal{H}_{rr} = \int \phi_r^* \mathcal{H} \phi_r d\tau = \alpha_r \qquad (1.2)$$

$$\mathcal{H}_{rs} = \int \phi_r^* \mathcal{H} \phi_s d\tau = \beta_{rs} \quad , r \neq s \qquad (1.3)$$

The one-electron energy levels ε_j may be shown by the variation principle to satisfy the eigenvalue equation

$$\underset{\sim}{\mathcal{H}}\,\underline{c}_j = \varepsilon_j \underset{\sim}{S}\,\underline{c}_j \qquad (1.4)$$

Where the elements of the overlap matrix $\underset{\sim}{S}$ are defined thus:

$$S_{rr} = \int \phi_r^* \phi_r \, d\tau = 1 \qquad (1.5)$$

$$S_{rs} = \int \phi_r^* \phi_s \, d\tau \qquad (1.6)$$

As a further approximation throughout the present work we take $S_{rs} = 0$, for all $r \neq s$ (neglect of overlap approximation)

So we have: $\underset{\sim}{S} = \underset{\sim}{1}$ (unit matrix) (1.7)

We may remove the need for a unit of energy by taking the value of α_r for a carbon atom in benzene (say) $= \alpha$ and β_{rs} for a carbon-carbon bond in benzene $= \beta$. We may thus express:

$$\alpha_r = \alpha + h_r \beta \qquad (1.8)$$

$$\beta_{rs} = k_{rs} \beta \qquad (1.9)$$

As the zero of energy is arbitrary we may take $\alpha = 0$ and the <u>secular equations</u> (1.4) then become

$$\underset{\sim}{H} \underset{\sim}{c}_j = m_j \underset{\sim}{c}_j \qquad (1.10)$$

$m_j = \epsilon_j / \beta$ being a pure number described hereinafter as an <u>energy parameter</u>, and $\underset{\sim}{H}$ now being a matrix whose elements are h_r and k_{rs} , which we shall call the <u>secular matrix</u>. The numbers m_j are thus seen to be the eigenvalues (in the algebraic sense) of the matrix $\underset{\sim}{H}$ and the $\underset{\sim}{c}_j$ are the corresponding eigenvectors.

For hydrocarbons we may take as a first approximation all the <u>atom parameters</u> h_r to be equal ($=0$), all the <u>bond parameters</u> k_{rs} for neighbouring (bonded) atoms to be equal ($=1$), and all other k_{rs} zero. In these special circumstances only, the matrix $\underset{\sim}{H}$ becomes the <u>topological matrix</u> of the molecule. In the present work molecules with all $h_r = 0$ and all $k_{rs} = 1$ are called <u>hydrocarbons</u>, an atom with $h_r \neq 0$ is called a <u>heteroatom</u>, a bond with $k_{rs} \neq 1$ a <u>heterobond</u>

and a molecule with one or more heteroatoms or heterobonds is called a heteromolecule.

1.1. Neglect of overlap approximation.

The value of the overlap integral Srs for two 2pπ orbitals at usual aromatic ring distances is about 0.25. Its neglect can thus not be justified on grounds of numerical size. However it may be shown (see e.g. Chirgwin and Coulson 1950) that many quantities derived from molecular orbitals are very little changed by using a full treatment where S is not neglected. Only in this way do we justify the extensive use of the simpler method. Chirgwin and Coulson also showed, as had Wheland (1941) by a different method, that the energy levels which arise from a full treatment when S is included may be derived from those obtained from the simple treatment by use of the formula:

$$E_j = \frac{\alpha + m_j\beta}{1+m_j S} = \alpha + \frac{m_j(\beta - \alpha S)}{1+m_j S} = \alpha + k_j\gamma \qquad (1.11)$$

where $\gamma = \beta - \alpha S$, $k_j = \frac{m_j}{1+m_j S}$

2. Quantities derived from Huckel molecular orbitals.

We have mentioned above the energy levels and the molecular orbital coefficients. From these several other quantities may be calculated which have been introduced by various workers to facilitate correlations with chemical and physical properties of the molecules being considered.

The first of these is the total π-energy. If electrons are allowed to occupy the molecular orbitals two at a time starting at the lowest, which is the one with the greatest m_j since β is negative, and the

and a molecule with one or more heteroatoms or heterobonds is called a heteromolecule.

1.1. Neglect of overlap approximation.

The value of the overlap integral Srs for two $2p\pi$ orbitals at usual aromatic ring distances is about 0.25. Its neglect can thus not be justified on grounds of numerical size. However it may be shown (see e.g. Chirgwin and Coulson 1950) that many quantities derived from molecular orbitals are very little changed by using a full treatment where S is not neglected. Only in this way do we justify the extensive use of the simpler method. Chirgwin and Coulson also showed, as had Wheland (1941) by a different method, that the energy levels which arise from a full treatment when S is included may be derived from those obtained from the simple treatment by use of the formula:

$$E_j = \frac{\alpha + m_j\beta}{1 + m_j S} = \alpha + \frac{m_j(\beta - \alpha S)}{1 + m_j S} = \alpha + k_j\gamma \qquad (1.11)$$

where $\gamma = \beta - \alpha S$, $k_j = \frac{m_j}{1 + m_j S}$

2. Quantities derived from Huckel molecular orbitals.

We have mentioned above the energy levels and the molecular orbital coefficients. From these several other quantities may be calculated which have been introduced by various workers to facilitate correlations with chemical and physical properties of the molecules being considered.

The first of these is the total π-energy. If electrons are allowed to occupy the molecular orbitals two at a time starting at the lowest, which is the one with the greatest m_j since β is negative, and the

corresponding energy eigenvalues are added up a total π-energy is obtained which may be correlated with the thermodynamic stability of the molecule.

The next group of quantities comprises charges, bond orders and polarisabilities. These are all described, the latter being introduced, in Coulson and Longuet-Higgins (1947).

The π-electron density or charge q_r on atom r of a conjugated system is defined by:

$$q_r = \sum_j \nu_j c_{rj}^2 \qquad (2.1)$$

The summation is over all molecular orbitals j ν_j being the number of electrons in the jth orbital. The charge is a useful index for comparing reactivity towards electrophilic reagents, it may also be used for estimating π-dipole moments.

The π-bond order prs for the pair of atoms r,s is defined by:

$$p_{rs} = \sum_j \nu_j c_{rj} c_{sj} \qquad (2.2)$$

for bonded atoms it may be used as a measure of the 'double-bond character' of the bond r-s. It is thus also related to the bond length . For any pairs of atoms, whether or not bonded, it has been shown by Pople (1953) that prs measures the correlation in position between electrons of similar spin.

Note: For a molecule with 2m electrons $\nu_j = 2$ for $j \leq m$, 0 for $m+1 \leq j \leq n$

For a molecule with 2m+1 electrons $\nu_j = 2$ for $j \leq m$, 1 for $j = m+1$, 0 for $m+2 \leq j \leq n$

except in those cases where the highest occupied orbital is degenerate i.e. several orbitals have the same energy parameter. In these cases ν_j is

calculated by considering a suitable fractional number of electrons in each orbital of the degenerate set so that the total number of electrons is accounted for. This process of equalization ensured that the charge distribution and bond orders shall have the full molecular symmetry. This method of dealing with degenerate cases is the simplest and is consistent with the general assumptions of the method. Any fuller treatment would have to take into account the Jahn-Teller effect (Jahn and Teller 1937) whereby the molecule distorts so as to remove the orbital degeneracy (see also Streitwieser (1961) p.53).

Bond orders are also used to calculate free Valences of atoms. If the π-bond orders for all bonds to the atom r are added and the total subtracted from a theoretical maximum which is usually taken to be $\sqrt{3}$ we obtain the free valence Fr of atom r

$$F_r = \sqrt{3} - \sum_s p_{rs} \quad (s \text{ all neighbours of } r) \qquad (2.3)$$

As its name implies Fr is useful as a measure of reactivity towards free radicals.

In order to estimate how charges and bond orders change when the coulomb terms α_r and resonance integrals β_{rs} are altered Coulson and Longuet-Higgins (1947) introduced the polarizabilities defined thus:
(We have used h_s, k_{st} instead of α_s, β_{st} in order to make the quantities dimensionless).

$$\begin{aligned}
\pi_{r,s} &= \text{atom-atom polarizability} = \partial q_r / \partial h_s \\
\pi_{r,st} &= \text{atom-bond} \quad " = \partial q_r / \partial k_{st} \\
\pi_{st,u} &= \text{bond-atom} \quad " = \partial p_{st} / \partial h_u \\
\pi_{rs,tu} &= \text{bond-bond} \quad " = \partial p_{rs} / \partial k_{tu}
\end{aligned} \qquad (2.4)$$

Coulson and Longuet-Higgins gave two sets of formulae for these quantities: the first involving contour integrals is less suited to automatic computation than the second, obtained by a straight forward application of perturbation theory, which are:

$$\pi_{r,r} = 4\sum_{j=1}^{m}\sum_{k=m+1}^{n}\frac{c_{rj}\,c_{rk}\,c_{rj}\,c_{rk}}{m_j - m_k} \qquad (2.5)$$

$$\pi_{r,rs} = 4\sum_{j=1}^{m}\sum_{k=m+1}^{n}\frac{c_{rj}\,c_{rk}\,(c_{rj}\,c_{sk} + c_{sj}\,c_{rk})}{m_j - m_k} \qquad (2.6)$$

$$\pi_{rs,rs} = 2\sum_{j=1}^{m}\sum_{k=m+1}^{n}\frac{(c_{rj}\,c_{sk} + c_{sj}\,c_{rk})(c_{rj}\,c_{sk} + c_{sj}\,c_{rk})}{m_j - m_k} \qquad (2.7)$$

$$\pi_{rs,r} = 2\sum_{j=1}^{m}\sum_{k=m+1}^{n}\frac{(c_{rj}\,c_{sk} + c_{sj}\,c_{rk})\,c_{rj}\,c_{rk}}{m_j - m_k} = \tfrac{1}{2}\pi_{r,rs} \qquad (2.8)$$

The changes in α and β may either be permanent as when one is calculating the effect of introducing a heteroatom or a substituent with an inductive effect, or they may be temporary as when considering intermediates which might be of importance in chemical reactions. Because of the latter, polarizabilities are sometimes useful as indices of reactivity. The polarizabilities $\pi_{r,r}$ and $\pi_{rs,rs}$ are called <u>self-polarizabilities</u> for atom r and bond rs respectively.

Many other quantities may be calculated from Hückel molecular orbitals - few, however, are of such general applicability as those mentioned above.

<u>3. The dictionary of π-electron calculations.</u>

The motivation for the present work was the need for a set of tables of Hückel molecular orbitals and derived quantities which would be available to all chemists, practical as well as theoretical, who wished to use these quantities. As the number of molecules to which the method may be applied is, of course,

infinite, an arbitrary restriction of the size of such a book must be made. The first compilation of this sort was a privately produced set of tables, all of which had been calculated by hand or on desk machines by the authors and other workers, which was produced by Professors Coulson and Daudel in 1954. A Second edition was started in 1959, but by 1961 it was realized both by Professor Coulson and independently by Professor Streitwieser at Berkeley, California, that a printed edition containing tables calculated on a computer could usefully be produced. The programmes to be described in the present thesis were written primarily to produce such tables for direct photolithographic reproduction.

Professors Coulson and Streitwieser had had different ideas of how big their books should be. Professor Streitwieser decided on a very large compilation containing tables for all the quantities described above for most of the known hydrocarbon systems containing less than 20 π-electrons and many containing more. Professor Coulson decided on a smaller volume giving complete tables only for the commonest molecules, but in addition to hydrocarbons, giving tables for certain very common hetero-systems with a selection of values for the parameters h, k which have to be chosen empirically for any particular heteromolecule.

The two authors have collaborated and the Dictionary of π-electron calculations to be published by Pergamon Press in 1965 is to appear under both names. The second book : Supplemental Tables of

Molecular Orbital Calculations will contain the rest of Professor Streitwieser's calculations and will appear under his name only. So, although the tables in the Dictionary of π-electron Caloulations have been prepared exclusively using my programmes, all the calculations have also been carried out independently at Berkeley by Professor Streitwieser and his collaborator J.I.Brauman. These have been useful in providing a check on most of the quantities calculated.

4. The problems of producing a book of tables.

The most important quality required of a set of tables is that the numbers tabulated shall be accurate. If we assume for the moment that they have been calculated by a suitable numerical procedure from mathematical formulae whose correctness is not in doubt, the chief requirement is that there shall be no copying mistakes between the calculating machine and the printed page. Humans are notoriously fallible at such tasks and one must if possible have the entire process done by machines of various sorts - the fewer different stages the better. The actual calculations are done on the Mercury computer at the Oxford University Computing Laboratory. This machine has only one form of output - 5-hole punched paper tape. This is normally converted into printed characters on paper by a Creed teleprinter. This immediately imposes two limitations on the output - the number of characters in a line must not exceed 68 and the range of characters is limited to those available on the teleprinter. These are the 26 upper-case letters of the Roman alphabet, the digits 0-9 and certain punctuation and mathematical symbols.

Having produced a single-copy set of printed tables on the teleprinter, each page may be photographed by the photo-litho camera and so converted into a printing plate. All stages beyond the production of the first set of tables on special paper suitable for photolithography were in the present case done by the printers and publishers.

Certain safeguards against errors are inherent in the above system. The five-hole tape code is such that all digits are represented by an odd number of holes; thus, if a single hole in a character should fail to be punched, an immediately recognizable error in the form of a symbol other than a digit will appear. It is unlikely for two holes to be mis-punched in the same character, and, a fortiori, exceedingly unlikely that such an error would occur without a 'single' error in the same tape; so, if one adopts a policy of reprinting (if it is the teleprinter that is misbehaving) or recomputing (if it is the output punch of the computer) whenever such a mispunching error occurs, the overall risk of a wrong digit in the final print-out is so small as to be acceptable.

A fault of the output punch on the computer which was prevalent at the time these computations were done was "double-punching" - the punching of a single character two or more times when it should appear only once. This made itself obvious immediately because numbers were arranged to have standard

numbers of digits and as all the output was laid out in tabular form these errors caused the right-hand margin to be irregular. As machine time was very short and this fault sometimes less frequent than at others, the policy of only recomputing when more than about 5 such errors occurred in the tables for one molecule was adopted. When only a few such errors occurred one of the repeated characters was covered with adhesive tape; this is a practice not to be recommended as it is easy to cover up the wrong character and produce a table which looks all right but contains a wrong digit. Very careful checking of these cases was thus done and any cases where it was ambiguous which character had been double-punched were recomputed.

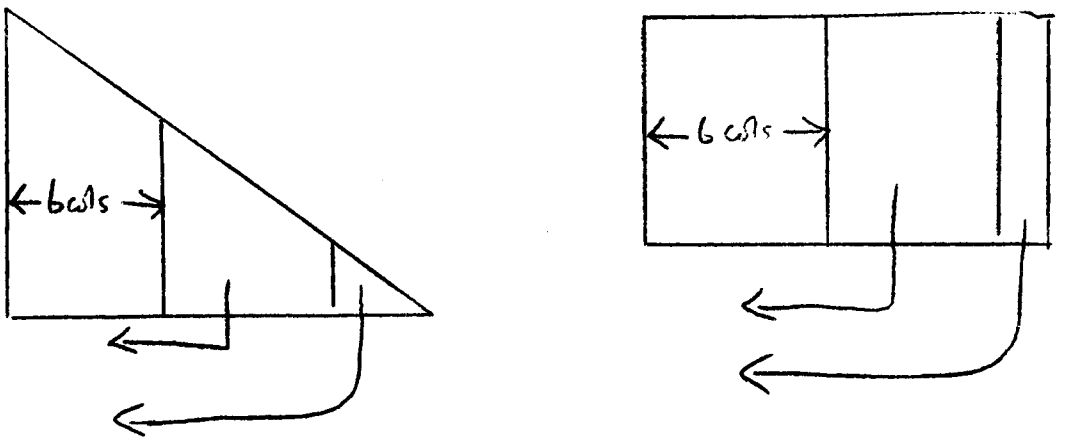
5. Intelligibility of the tables.

If we assume now that we have devised a process for converting punched paper tape in Ferranti Code into printing plates, we can turn our attention to the layout of the results and the main logical structure of the programme required to produce the tape.

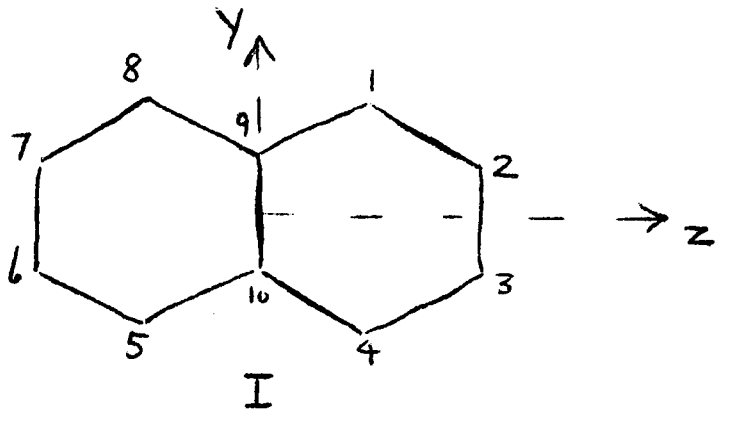
A very important feature of a book of tables is that it must be easy for a user to discover whether what he wants is present and, if it is, to find it quickly and without ambiguity. The first requirement can be satisfied by arranging the molecules in some sort of order and providing adequate indices; the second requires that for each molecule the results shall be tabulated in a standard way with each table

clearly labelled to indicate what quantities are being tabulated.

Two types of tables have been used - columns and matrices, the rows of these and the columns of the latter being preceded by labels to indicate the atom, bond or orbital concerned. Each table is headed by the name of the quantity being tabulated. Two methods of displaying matrices have been used, depending on whether or not the matrix is symmetrical. In both methods a matrix with more than 6 columns is split into blocks of 6 full-length columns succeeding blocks being placed below one another on the page. If the matrix is symmetrical only the lower triangle is shown, each block then being 6 rows shorter than the one above. If the matrix is rectangular all blocks will have the same number of rows.



6. Use of molecular symmetry to reduce size of tables.



I

All physical observables for a molecule must be

invariant under all the symmetry operations of the molecule; e.g. for naphthalene I all numerical quantities connected with atom 1 also apply to atoms 4,5,8 and similarly for bonds related by symmetry. In fact for quantities concerned with one atom at a time we need tabulate only the values for atoms 1, 2 and 9. These will be referred to as <u>selected atoms</u>. For quantities concerned with one bond at a time we need tabulate only for the <u>selected bonds</u> 1-2, 1-9, 2-3 and 9-10. For quantities connecting two atoms, two bonds or an atom and a bond the simplest general method of tabulation is to have a matrix which has (say for an atom-atom quantity in molecule I) columns for the atoms 1,2,9 and rows for all the atoms. To eliminate the repeated tabulation of the same numerical quantity that this produces (e.g. 2-5 and 1-6) is not practicable.

Besides 'atom' and 'bond', the other type of label that can appear is 'orbital' and in the case of alternant hydrocarbons it may be shown that these also possess a symmetry in that the unoccupied anti-bonding orbitals are complementary to the occupied bonding orbitals. An <u>alternant</u> molecule is one where the atoms may be divided into two sets, starred and unstarred, such that no two members of one set are adjacent. Such molecules thus comprise all those being treated in the present work which do not contain rings of odd numbers of atoms. From any bonding orbital j with energy parameter n_j and eigenvector ξ_j of coefficients the <u>complementary</u> orbital has energy parameter $-$ and has an eigenvector

derived from ζ_j by changing the sign of all coefficients belonging to one set (say starred) of atoms. For such molecules it is then unnecessary to tabulate the anti-bonding orbitals. As the orbitals are not themselves observables the coefficients are not invariant under the symmetry operations of the molecule. Their squares, however, being associated with electron density, are invariant and so the coefficients of atomic orbitals related by symmetry can differ only by a factor ± 1. A label to indicate whether this factor is +1 or -1 for a given orbital will suffice to determine all the coefficients if only those for 'selected' atoms are given. This division of orbitals into sets belonging to different symmetry species will be described more fully below.

7. Logical structure of the programme used to compute quantities derived from Hückel molecular orbitals.

The programme to be described in the present section forms Chapters 3,4 and 5 of all versions of the HMO programme. Chapters 0 and 1 concern the input of data and calculation of the energy parameters and eigenvectors and Chapter 2 concerns the tabulation of these.

Which quantities are to be calculated and tabulated for a given molecule is determined by the values of the parameters Vn, Wn, Xn, Yn and Zn read in as data. The choice of values for these by the user is described in appendix A to this chapter. Here we give the interpretation by the programme of all possible values of these parameters.

1. Vn Charge/Bond order parameter

≤0.5 No charges/bond orders printed.

If Wn > 0.5, bond orders for all bonds are calculated.

>0.5 <1.5 If 'selected bonds' have been defined: prints column of Bond orders for selected bonds.

If 'selected bonds' have not been defined: prints column of Bond orders for all bonds.

>1.5 <99 As above but also a column of charges for 'selected atoms' if defined otherwise for all atoms.

>99 <250 Rectangular charge-bond order matrix: Rows- all atoms. Columns- selected atoms.

≥250 Complete lower triangle of symmetrical charge bond-order matrix.

2. Wn ≤0.5 No free valences calculated or printed.

>0.5 Column of free valences tablulated for atoms as for charges when Wn=2 (above)

3. Xn, Yn, Zn Polarisabilities.

The quantities tabulated are the negative of those defined in equations 2.5, 2.7, 2.6. This is because β is negative. As tabulated a positive polarizability means that the charge (bond order) increases when the coulomb term or resonance integral is increased algebraically

Xn AA ≤0.5 No polarisabilities calculated or printed.

Yn BB >0.5 <1 NOT ALLOWED. (prints: ATOM-ATOM or BOND-BOND and calls for 1024 items of data).

≥1 ≤92 If there is a list of INTPT $\binom{Xn}{Yn}$ pairs of numbers at end of data tape will read these in blocks ≤46pairs, calculate and print. (INTPT = integral part of).

92 Calculates and tabulates in a column
100.5 self-polarisabilities ($\frac{\pi_{r,r}}{\pi_{rs,rs}}$) for
selected (atoms) if set, otherwise for all.
(bonds)

> 100.5 ditto. ditto.) Then subtracts
< 101 " ") 100 and reads
> 101 " ") list as above.
< 195 " ")

> 195 Rectangular matrix : columns- selected (atoms)
(bonds)
rows - all (atoms)
(bonds)

> 250 Triangular matrix : rows and columns
- all (atoms)
(bonds)

Zn AB.

< 92 as Xn, Yn

> 92 as 92
< 195
> 195 } Rectangular matrix: rows - all bonds
< 250 } columns - selected atoms

> 250 Rectangular matrix rows - all bonds
columns - all atoms.

We now give a simplified flow diagram to indicate how this has been implemented. This may be compared with the Autocode programme in appendix B to this chapter.

Chapter 3 contains all parts concerned with charges, bond orders and free valences, except for the tabulation of matrices which is in Chapter 4 and is entered as a subroutine when necessary. Also in Chapter 4 are the subroutines for calculating polarisabilities and organising the calculation of matrices of polarisabilities. Chapter 5 is the general organising chapter for the polarisabilities.

FLOW CHART 1 **Calculation of derived quantities**

from Chapter 2

40)

Un = Vn + Wn

YES

99 > Vn

NO

Print title : CHARGE - BOND ORDER MATRIX

Compute elements of Ch-BO. matrix by colum

250 > Vn

YES

NO

Triangular tabulation

12)

Rectangular tabulation

} Chapter 4 as sub-chapter

39)

Un = Wn

42)

YES

0.5 ≥ Un

NO

1.5 ≥ Vn

YES

NO

47)

Compute bond orders

0.5 ≥ Vn

YES

NO

Compute free valences

55)

0.5 ≥ Vn

YES

NO

Print title: BOND ORDERS

1.5 ≥ Vn

YES

NO

Print title: CHARGES

60)

0.5 ≥ Vn

YES

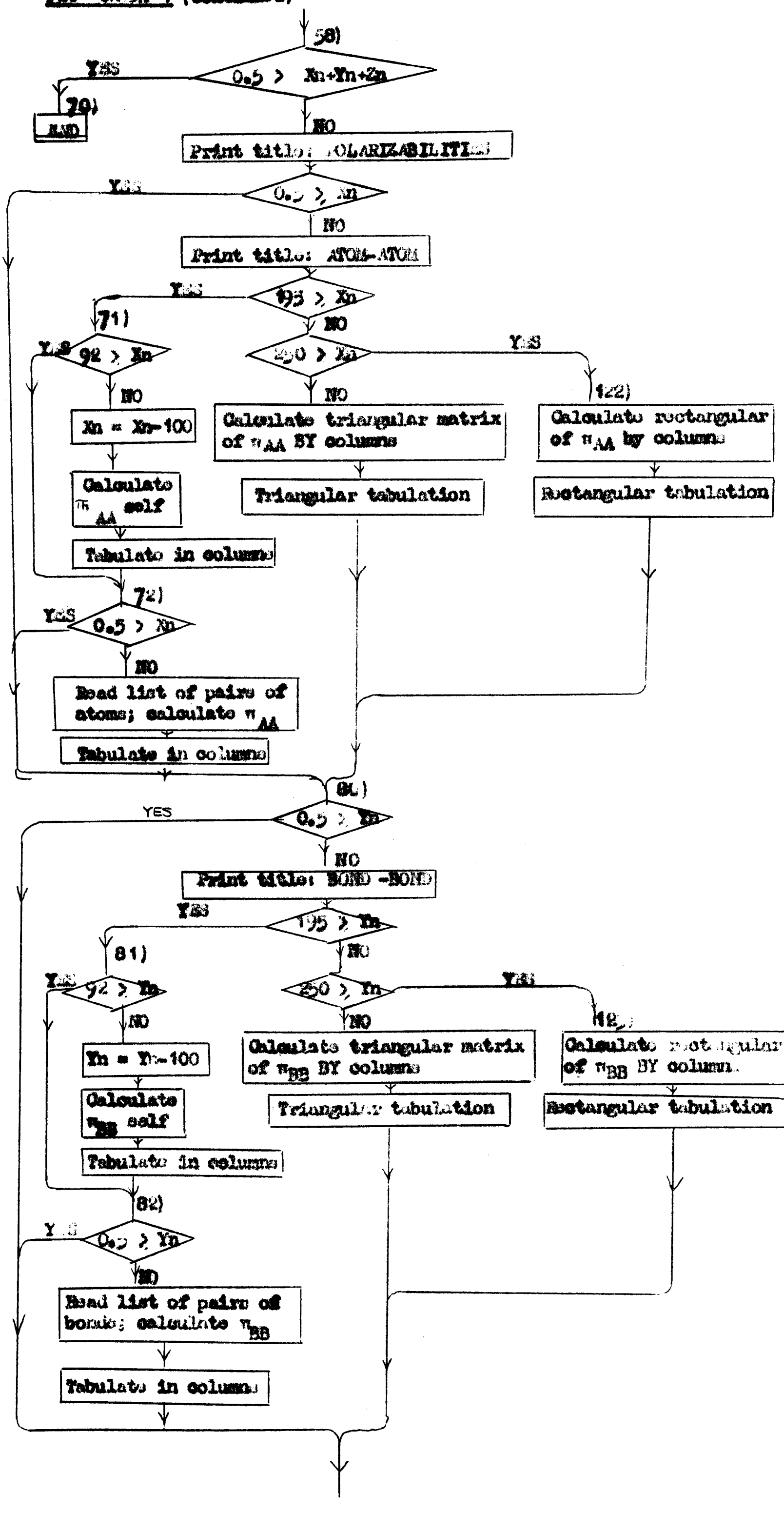
NO

Print title: FREE VALENCES

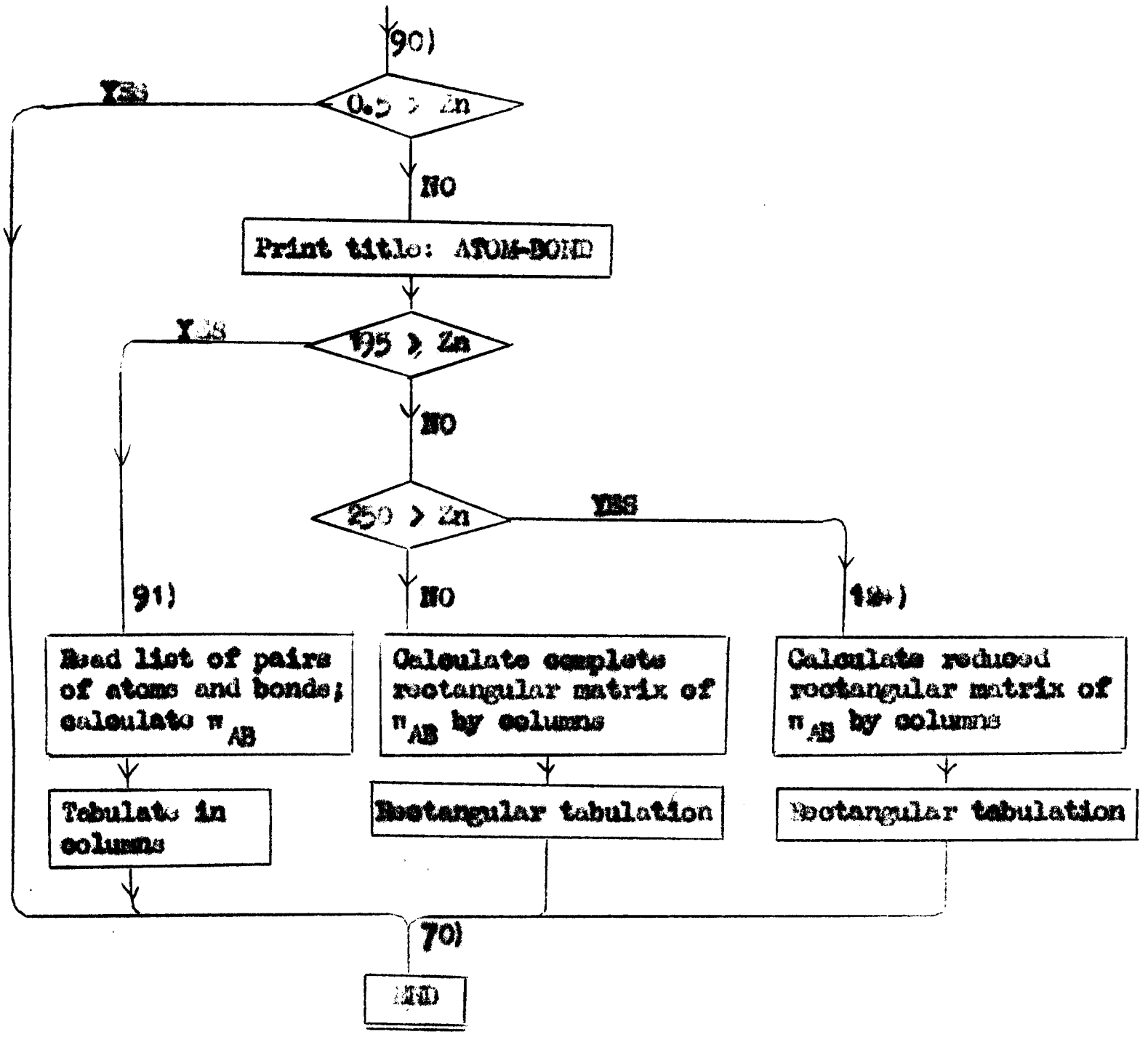
61)

Tabulate: Bond orders - charges - free valences in 3 columns side by side with bond/atom numbers at left of each column. (Omitting any column as in titles above)

FLOW CHART 1 (continued)



FLOW CHART 1 (continued)



8. The Data for different versions of the HMO Programme

As the programmes were to be used for many molecules, and possibly by persons other than the author, it was necessary to decide on standard formats for the data which would be simple to prepare, and to design programmes to read it accordingly.

Three sorts of information need to be provided to define the calculation for a particular molecule.

(i) Definition of the topology of the molecule and the values of any matrix elements (h_r and S_r)

(ii) Description of the symmetry(if any) of the molecule so that economies may be made in the size of tables produced (and also in the calculation - see below).

(iii) Parameters indicating which quantities are to be calculated and printed.

As the time taken to calculate the eigenvalues and eigenvectors of a matrix is proportional to n^3 it is advantageous to make use of the symmetry of a molecule to reduce the problem to that of diagonalising several smaller matrices since:

$$\sum n_i^3 < \left(\sum n_i\right)^3$$

As programme/input is slow on Mercury (a chapter can take up to about $\frac{3}{4}$ min. to read in) it was advantageous to write different versions of Chapters 0,1 and 2 for molecules with different symmetry, rather than to incorporate all versions into one large programme.

However, as it is not essential to make use of symmetry a programme which does not do so may be used

for any molecule. Version S was designed with this end in view, incorporating facilities for printing symmetry labels with orbitals, and using symmetry to reduce the size of tables, but starting with a completely general description of the molecular topology.

Version H. For hydrocarbons only. Symmetry is not used to speed-up the calculation.

Version E. As H, but one type of heteroatom and one type of heterobond must be present. Calculations may be repeated for different values of h_r and k_{rs} for these without re-reading all the data.

Version C. For Molecules with symmetry C_{2v} or C_{2h}. Two matrices corresponding to the two symmetry species are set up. Heteromolecules are permitted.

Version D. For Hydrocarbons with D_{2h} symmetry. Four matrices are set up. Heteromolecules are not permitted.

All versions will accept most appropriate molecules with up to 60 π-electron centres. Most limitations on size etc. mentioned in the notes (Appendix A) are imposed by the size of the working store of the computer. Larger molecules would have been possible if the programmes had been written in a language which permitted full use of the possibility of packing four integers into a Mercury word. In the Autocode language, the reasons for using which are mentioned in section 12.1 only 12 such integers (the

Indices) may be used at any one time and so long lists of integers have had to be stored as floating-point numbers.

In order to facilitate the compilation of data for any molecule, duplicated forms have been prepared for each of the 5 versions of the programme. By preparing the data on one of these forms one can be sure that all relevant numbers are included.

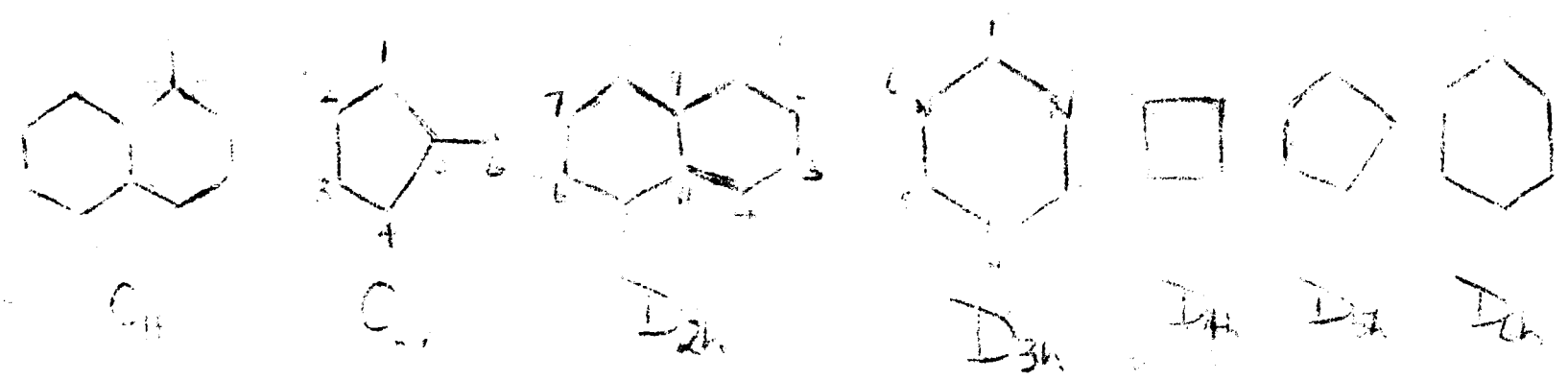
The data for all versions starts with a <u>heading</u> which is reproduced on the output up to but excluding a terminating character 'n' or '?'. This will usually comprise the name of the molecule and anything else necessary to define the particular calculation.

The next stage in preparing the data is to make a numbered drawing of the molecule. The system of numbering is arbitrary except that for a molecule with N π-centres the integers 1 to N must be used in some order. It is thus usually possible to conform to the usual chemists' numbering system except where this includes letters and primed numbers. It was not considered worth the extra difficulties of programming (one would not have been able to use the Autocode language) which would have been involved, if these were to be included. The absence of Greek letters and of a prime among the character setrules out a large number of such numberings at the outset.

8.1 <u>Numerical description of molecular symmetry.</u>

The molecules with which we are concerned all

contain at least one plane of symmetry - the nodal plane of the π-orbitals. The symmetry elements which are of importance for the present calculations are axes or planes of symmetry perpendicular to this nodal plane or a centre of symmetry (in the nodal plane). Examples of possible symmetry groups are given below:-



It is obvious from the diagrams that the groups D_{nh} may be considered as C_{2v} if n is odd or as D_{2h} if n is even. In fact any attempt to take full account of higher symmetry involves one in complex numbers which would involve complete rewriting of the programme and trouble in devising a way to present the complex orbitals neatly in tabular form. This is the reason that only the groups $C_{1h}, C_{2v}, C_{2h}, D_{2h}$ need be considered when designing the programmes. But, as the higher symmetry can be used to reduce the size of tables of derived quantities even when complex orbitals are not used, Version S, H and E permit the specification of lists of 'selected' atoms and bonds in the data quite independent of any description of the symmetry which may be given. The opposite policy is adopted in versions C and D and the programme generates its own lists of selected atoms and bonds.

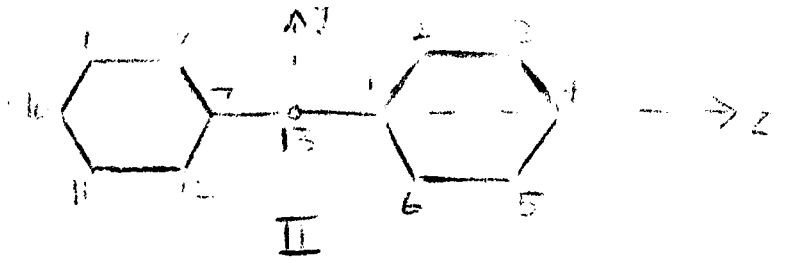
In order to describe the symmetry of a molecule in a numerical form suitable for the computer, one must divide the atoms into types - those at points through which no symmetry elements pass, those on each of the symmetry elements, and those on more than one symmetry element. For D_{4h}, the most complicated group we need consider, this gives four types. As an example we consider the molecule diphenyl-methyl II:

(a) atoms in general positions e.g. 2,3

(b) atoms on z-axis e.g. 1,7

(c) atoms on y-axis (none in this molecule)

(d) atom at the origin.



II

For C_{4v} and C_{4h} there are two types

(a) atoms in general positions

(b) atoms on the symmetry element.

If within each type we write each set related by symmetry in order anti-clockwise from + we get for the full symmetry description (for each type we have first the number of sets of that type):

2

2 8 12 6 general sets
3 9 11 5

2

1 7 } pairs on C_z
4 10 }

0 pairs on C_4

1

13 atom at origin

In Version D the list of 'selected' atoms is the list comprising the first number of each set. In this case: 2 3 1 4 13.

8.2 Definition of the topology of the molecule.

This part of the data, which includes the values of any matrix elements h_r and k_{rs} not equal to 0 or 1 respectively, is used by the programme to set up the secular matrix or matrices $\underset{\sim}{H}$. For versions S, H and E it consists of a list of pairs of nos. representing the atoms joined by the bonds in the molecule, with the appropriate value of k_{rs} if necessary, followed by a list of other non-zero matrix elements in the form row-column-value, remembering that as the upper triangle of $\underset{\sim}{H}$ only is set up the row no. must be $\leq$ the column no.

For versions C and D where the situations of the atoms relative to the symmetry elements have already been described, the minimum data to enable the computer to set up the matrices would be a list of 'selected' bonds, the operation of the symmetry elements on which would produce all the bonds of the molecule. This method has not been used, however, as the alternative method of dividing bonds into types, according to the 'types' of atoms they join, leads to simpler programming. This will be described more fully below (section 9.1).

8.3 Parameters indicating which quantities are to be calculated and printed.

The interpretation by the programme of the values of the parameters Vn, Wn, Xn, Yn, and Zn has been

described above. The other parameter which precedes these on the data tape for all versions of the programme is Un, which determines the printing of energy levels and orbitals. These quantities are tabulated in two tables. First a pair of columns giving the energy parameters m_j and k_j (eqns 1.10 and 1.11) where j can include all orbitals or merely those which are occupied; at the foot of this table is given the total π-energy E_π, the number of π-electrons in the molecule being assumed to be the number of π-centres unless otherwise given. Second a matrix of orbital coefficients c_{rj}: Each column of this matrix represents an orbital and the coefficients themselves are headed by an ordinal no. (lowest orbital, i.e. that with greatest m_j, =1) the energy parameter m_j and, if appropriate, a label indicating the symmetry of the orbital. The rows of the matrix are preceded by the atom numbers and correspond to those atomic orbitals from which a complete set may be derived using the symmetry (the 'selected' atoms).

The interpretation by the programme of values of Un is as follows:

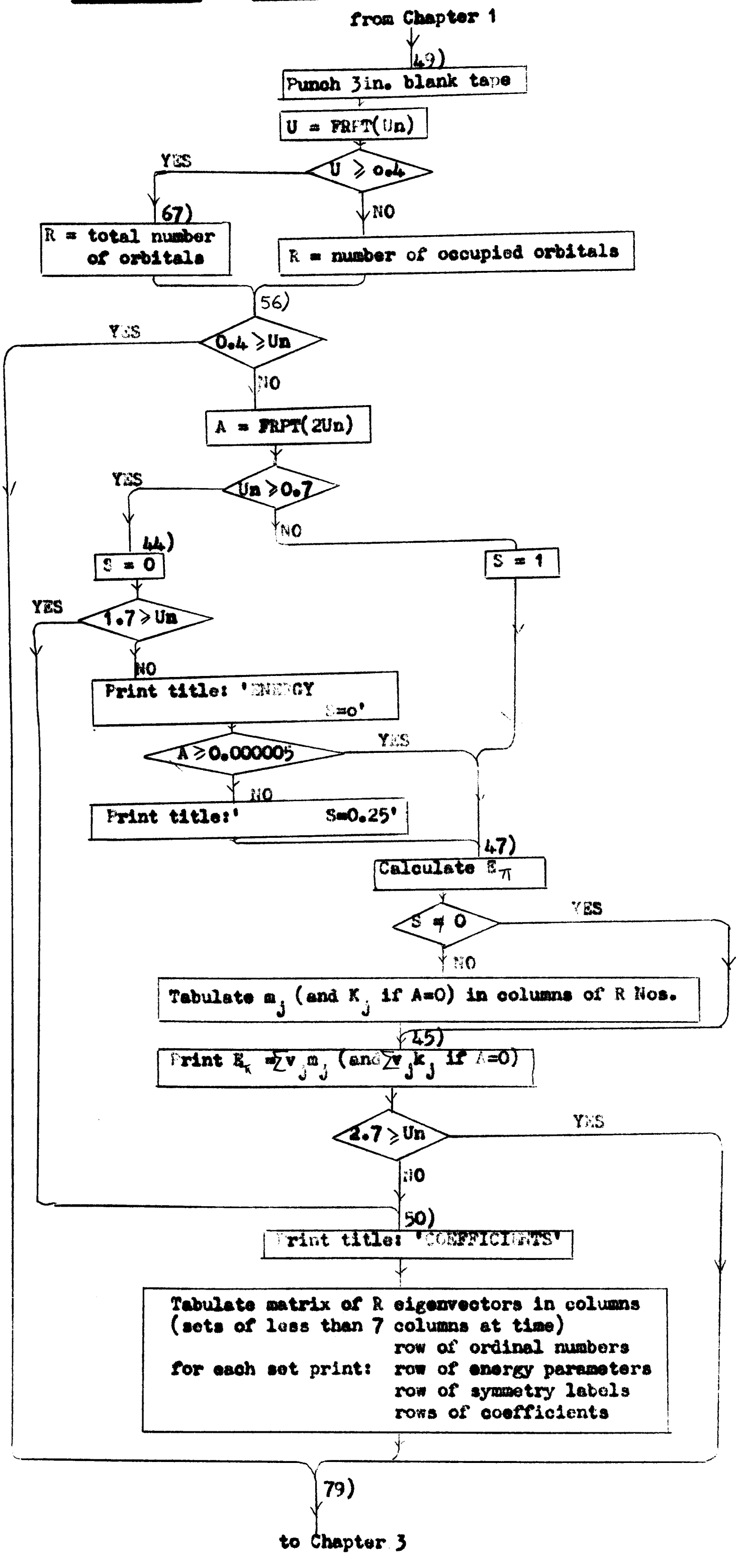
N.B. U = fractional part of Un, A= fractional part of 2Un

$Un \leqslant 0.4$	No energies or coefficients printed.
> 0.4 and $\leqslant 0.7$	Total π-energy only. Overlap-included value omitted if $A \geqslant 0.000005$

≥ 0.7, < 1.7	Coefficients table only printed.	If U $\geq$ 0.4 all orbitals quoted If U $<$ 0.4 only occupied orbitals quoted
≥ 1.7, ≤ 2.7	Energy in columns only	As above according to value of A
> 2.7	Both tables printed	

Below is given a flow diagram indicating how this has been implemented.

FLOW CHART 2 **Chapter for printing energy and coefficients**



2. Diagonalization of the Secular Matrix H

N.B. In this section use is made of the concepts and some of the equations of group theory, especially with regard to point groups. Proofs of results quoted and further discussion may be found in any of the standard texts on the subject. e.g Altmann (1962).

The eigenfunctions of a Hamiltonian operator H may, and, in cases where there are no degeneracies, must, also be eigenfunctions of any other operator which commutes with H. Important in the present context among such operators are the symmetry operators which leave the molecule, and hence its Hamiltonian, invariant. The set of symmetry operators which leave a molecule invariant comprise a point group, and correspond to reflections in the planes, rotations about the a xes and inversions in the centres of symmetry already mentioned.

All the symmetry operators R in the point groups C_{2v}, C_{2h}, and D_{2h} with which we are concerned are such that $R^2=E$ (the identity). Such an operator can only have the eigenvalues 1 or -1. The molecular orbitals must thus be such that the coefficients of atomic orbitals on atoms related by the symmetry elements differ only by a factor of $\pm$ 1. The orbitals may thus be said to be either symmetric (S) or anti-symmetric (A) with respect to any such operation. When degeneracies occur among the eigenvalues (these may be forced by the presence of axes of symmetry of order

≥ 3, or may be 'accidental') any linear combination of the orbitals corresponding to the degenerate eigenvalue will be an eigenfunction, but it will be possible to derive from such an arbitrary combination orbitals which have these symmetry properties.

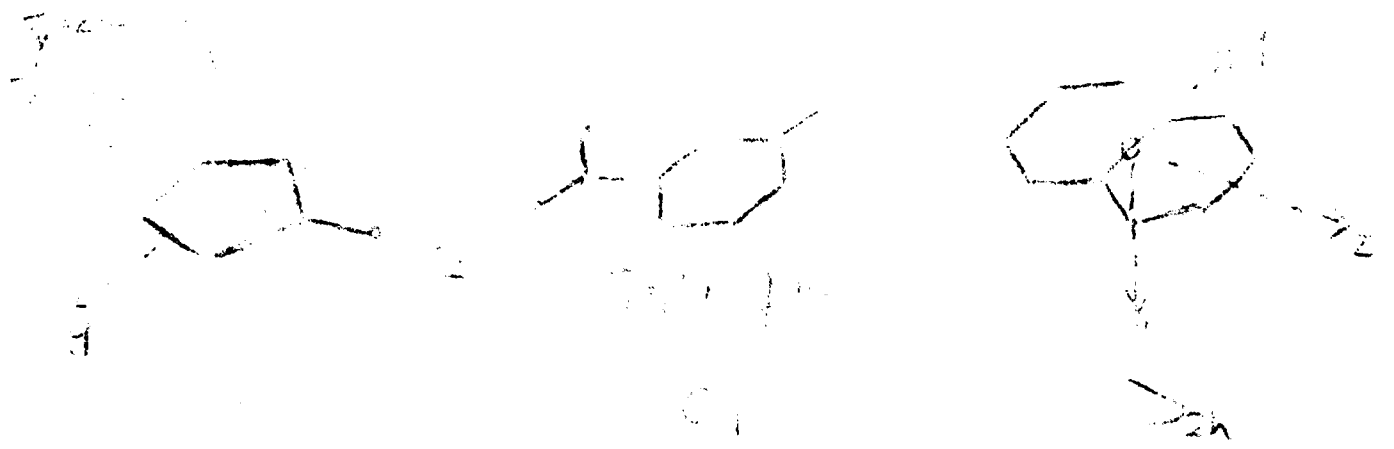
In the language of group theory we may say that each orbital is a basis for an irreducible representation of the point group, and may be said to <u>belong</u> to an irreducible representation. Tables of the characters of those representations of the groups C_{2v}, C_{2h} and D_{2h} which are of interest to us are given in table 1. Note that in these simple cases we may interpret the characters as indicating whether a function belonging to the representation is S (X = 1) or A (X = -1) with respect to each operation.

C_{2v}	E	σ_v	σ_v'	C_2
A_2 - As	1	-1	-1	1
B_1 -Ss	1	1	-1	-1

C_{2h}	E	C_2	σ_h	i
Au - .o	1	1	-1	-1
Bg - Ao	1	-1	-1	1

D_{2h}	E	σ_y	σ_z	C_2^x	σ_x	C_2^z	C_2^y	i
A_{1u} - Ayaz	1	-1	-1	1	-1	1	1	-1
B_{1g} - yAs	1	-1	1	-1	-1	1	-1	1
B_{2g} - Ayas	1	1	-1	-1	-1	-1	1	1
B_{3u} - yAs	1	1	1	1	-1	-1	-1	-1

Table 1. Character tables.



Only those irreducible representations have been shown which are antisymmetric with respect to reflection in the molecular plane (σ_v', σ_h, σ_x in C_{2v}, C_{2h}, D_{2h} respectively) as all π-orbitals must, by definition, be of these sorts.

Besides the usual group-theoretical names, a simple notation which describes directly the symmetries of the orbital coefficients is given.

It should be noted that these groups may be considered as direct products of the group C_{1h} with the groups C_{1h}, C_2 and C_{2v} in suitable orientations respectively. The dotted line in the table separates the cosets whose representatives are the elements E, σ_h of C_{1h} respectively.

Some possible confusion in the choice of names for the irreducible representations will be clarified by considering the principles on which they have been chosen.

(a) Orientation of the molecule relative to a set of cartesian axes. Molecules like Naphthalene with D_{2h} symmetry have been considered in the orientation used by spectroscopists. This has the unfortunate disadvantage that the atomic p orbitals which form the π-orbitals must be taken as p_x orbitals rather than the more usual p_z. To be consistent, this has been done throughout.

(b). Naming of planes of symmetry. A plane of symmetry perpendicular to a cartesian axis is most simply described (e.g. σ_x) with reference to that axis. This notation has been used at the top of the table. However, when a 2-dimensional drawing of a molecule

is used it can only easily be labelled with two axes Oy and Oz. A label such as AySz means that an orbital belonging to this representation is anti-symmetric with respect to reflection in the plane (at right angles to the molecular plane) containing the axis Oy (i.e σ_z) and symmetric with respect to reflection in the plane containing Oz (i.e σ_y).

(e) Simple names of representations in the group C_{2h}. The letters S and A are applied to a π-orbital if the coefficients of atomic orbitals related by the centre of symmetry are equal or equal but of opposite sign respectively. As the π-orbitals are antisymmetric in the molecular plane and so change sign on inversion in the centre of symmetry, S must be taken to mean "symmetric with respect to rotation about the 2-fold axis through the centre of symmetry", etc.

As has been mentioned above, provided that no degeneracies occur, the eigenvectors of the secular matrix $\underset{\sim}{H}$ will automatically belong to one of the irreducible representations. In order to determine which it is necessary only to examine the coefficients of atomic orbitals related by symmetry to see if they are equal, or equal but of opposite sign. This is the method used in Chapter 2 of versions S, H and E of the programme to determine which symmetry label to print. If by any chance an orbital occurs which does not show the required symmetry a label consisting of 3 asterisks is printed to draw the user's attention to this fact.

However, on account of the drastic nature of the approximations involved, accidental degeneracies among

the eigenvalues are not infrequent. One also wishes to be able to treat molecules where degeneracies occur because of the symmetry. As in these cases a programme to find eigenvalues and eigenvectors will in general give linear combinations of vectors belonging to the irreducible representations a method has to be devised to derive these from an arbitrary vector.

It should be noted that in order to obtain correct answers from the formulae for charges, bond orders, etc. it is necessary only that the vectors of a degenerate set be orthonormal. However it is often useful (e.g. in spectroscopic applications or for perturbation calculations) to have vectors which belong to the irreducible representations, and so the programmes have been written to produce these.

In order to derive from an arbitrary function ϕ its component function belonging to the i'th irreducible representation of a point group G one must apply the operator

$$V^i = \sum_{R \in G} \chi^i(R)\, R \qquad (9.1)$$ (Altmann 1962 -p.150)

where $\chi^i(R)$ is the character of the operation R in the representation i of G. A function ϕ^i belonging to this representation may be obtained by evaluating:

$$\phi^i = V^i \phi \qquad (9.2)$$

If ϕ^i is identically zero, this implies that ϕ does not contain a component belonging to the ith irreducible representation.

Since reflection of a molecular orbital in the plane of the molecule does not change it (any eigen-

function is unchanged by multiplication by an arbitrary constant) the groups G which we need consider when calculating ϕ^i's are the subgroups whose complete character tables are given to the left of the dotted lines in Table 1. The names of the representations are however retained from the larger groups as they are of interest to spectroscopists.

This method of deriving molecular orbitals belonging to the irreducible representations is used in Chapter 1 of version S of the programme. It will be referred to as <u>symmetrization</u> of molecular orbitals.

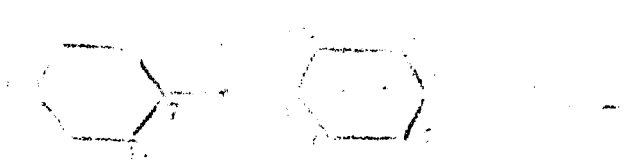
An alternative method of tackling the problem is to treat the various irreducible representations separately from the start by using as basis functions, instead of atomic orbitals, linear combinations (which may formally be derived by using the operators V^i) of these orbitals which belong to the irreducible representations. These functions are called symmetry-adapted functions. Now it is well known (e.g. Altmann (1962) p. 154) that matrix elements of any totally symmetric operator between functions belonging to different irreducible representations are identically zero. The secular matrix H thus reduces to the direct sum of several smaller matrices $\underset{\sim}{H}^i$ the sum of whose orders is the order of $\underset{\sim}{H}$.

<u>9.1 The problem of setting up the matrices $\underset{\sim}{H}^i$ from the data and the calculation of the molecular orbitals.</u>

The following discussion applies to the point group D_{2h}. A similar but very much simpler method

is applied to the smaller groups.

The symmetry-adapted basis-orbitals. Each set of 4 atoms in general positions gives rise to 4 symmetry-adapted basis orbitals - one belonging to each irreducible representation. Each pair of atoms on one of the cartesian axes gives rise to 2 basis orbitals - one belonging to each representation symmetric with respect to the plane containing that axis. An atom at the origin appears solely in the totally symmetric representation. As an example we give in Table 2 the symmetry-adapted basis orbitals for diphenyl-methyl



SySz	SyAz	AySz	AyAz
2+8+12+6	2+8-12-6	2-8-12+6	2-8+12-6
3+9+11+5	3+9-11-5	3-9-11+5	3-9+11-5
1+7		1-7	
4+10		4-10	
13			

Table 2. Symmetry-adapted basis orbitals

In these tables a combination such as 2+8+12+6 means the orbital $\frac{1}{2}(\phi_2+\phi_8+\phi_{12}+\phi_6)$ and similarly. All orbitals derived from 4 atoms have a normalization factor $\frac{1}{2}$, those from 2 one of $\sqrt{\frac{1}{2}}$.

As mentioned above the topology of the molecule can be described by dividing bonds into 'types' according to the 'types' of atoms they join. This is done as indicated in Table 3. Note the distinction between 'internal' and 'external' bonds.

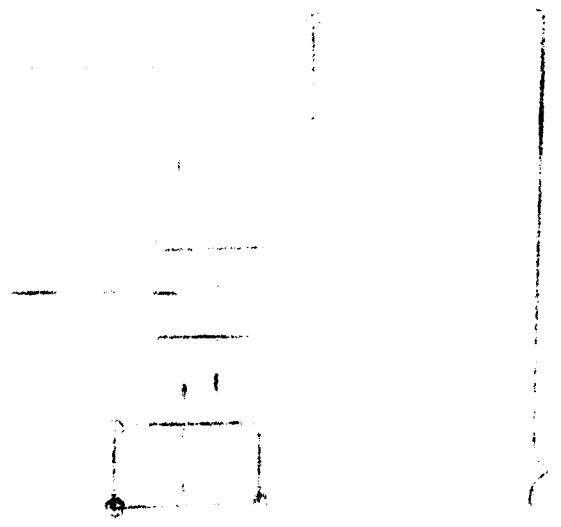
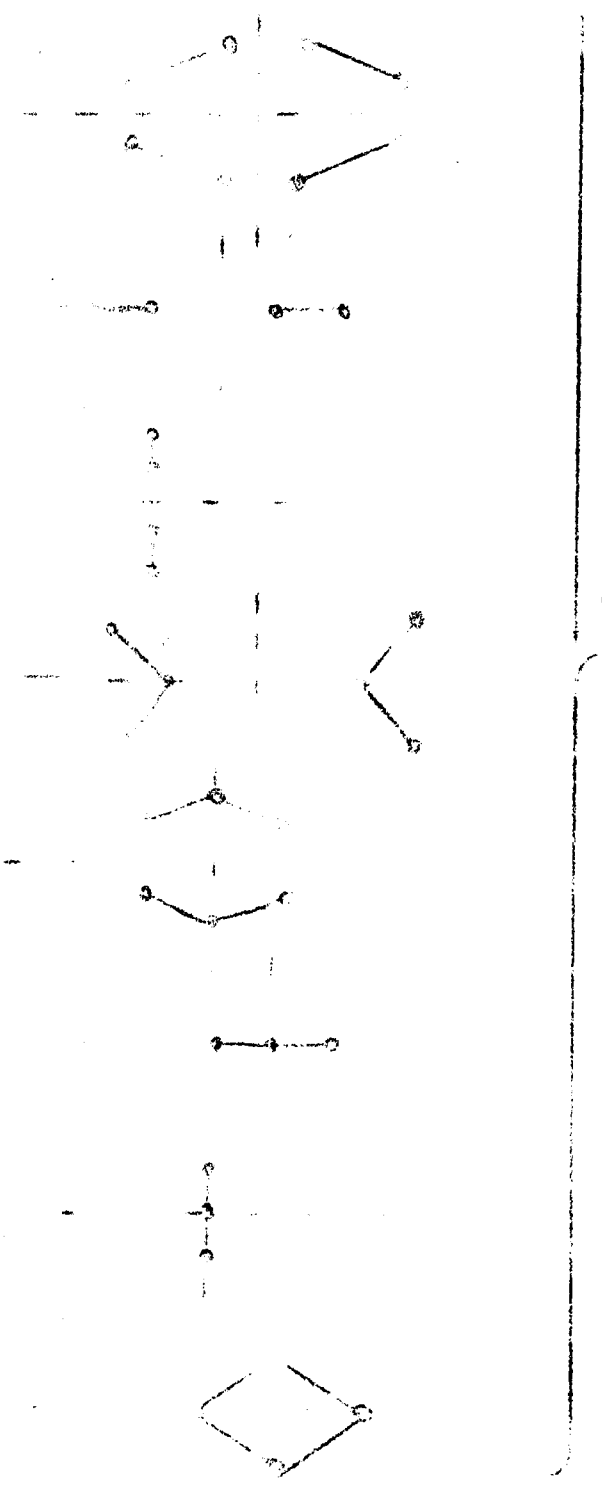
Atom types	Bond type	Example	
a - a	Ao		internal bonds.
	A1		
	A4		
b - b	A2		
c - c	A3		
a - a	Bo		external bonds.
b - b	B1		
c - c	B2		
a - b	B3		
a - c	B4		
b - d	B5		
c - d	B6		
b - c	B7		

Table 3. Bond Types.

The bonds in a molecule may be concisely described by giving the numbers of each type Ao-A4, Bo-B7 following each with a list of pairs of nos. These pairs are most conveniently the ordinal nos. (starting from 0 for computer convenience) of the sets of atoms as already listed. Thus for diphenyl-methyl the 'bond-list' takes the form shown in Table 4.

Ao	0	
A1	0	
A2	0	
A3	0	
A4	0	
Bo	1	
	0	1
B1	0	
B2	0	
B3	2	
	0	2
	1	3
B4	0	
B5	1	
	2	4
B6	0	
B7	0	

Table 4. Bond-list for diphenyl-methyl.

Each set of bonds gives rise to matrix elements in each matrix where symmetry-adapted basis-orbitals containing atoms involved in those bonds occur. The values of the matrix elements (which are added to the diagonal elements h for internal bonds) are given in Table 5 in units of /. In version D as it stands this can be only the standard / i.e. heteromolecules are not treated. It could however be any other / included with the bond in the data. In compiling this table careful account must be taken of normalization factors. An asterisk indicates that this type of bond does not give a matrix element of this symmetry species.

	SySz	AySz	SyAz	AyAz
Ao	1	1	-1	-1
A1	1	-1	1	-1
A2	1	-1	*	*
A3	1	*	-1	*
A4	2	0	0	-2
Bo	1	1	1	1
B1	1	1	*	*
B2	1	*	1	*
B3	/2	/2	*	*
B4	/2	*	/2	*
B5	/2	*	*	*
B6	/2	*	*	*
B7	2	*	*	*

Table 5. Values of matrix elements.

The matrices $\underset{\sim}{H}^{i}$ being set up using the numbers in this table their eigenvalues and eigenvectors may be found. It then remains only to generate a list of

all the eigenvalues in descending order and to convert the eigenvector coefficients to those appropriate for atomic orbital basis functions.

9.2 The subroutine for finding the eigenvalues and eigen-vectors of a matrix.

The Mercury Autocode Library includes a sub-programme - 517 which computes the eigenvalues and eigenvectors of a real-symmetric matrix by Givens' method (Givens 1954, Rollett and Wilkinson 1961). The method involves the conversion of the matrix, only the upper triangle of which is stored, to co-diagonal form by orthogonal transformation. (A co-diagonal or triple diagonal matrix C is one where elements C_{rs} are zero if $/r-s/ \geqslant 1$) The Sturm sequence property of the principle minors of this matrix (see e.g. Newman (1962) p.246) is then used to locate the eigenvalues, one binary digit at a time. The eigenvectors are found by Gaussian elimination and back substitution, followed by the inverse of the orthogonal transformation used in the first part.

Since the Sturm sequence method enables one to determine the i'th root for any given $i \leqslant n$ the roots may be found in order. This is very convenient for the present purpose.

There are two features of the library programme as available which have caused some troubles in the present work. Both are limitations which arise because our Secular matrices often have exact integer elements and can have exact integer eigenvalues and/or repeated eigenvalues. Eigenvalues of exactly zero

can lead to accumulator overflow (division by zero). Repeated eigenvalues (degenerate roots) give rise to non-orthogonal sets of eigenvectors. Zero eigenvalues may be avoided by adding to the matrix a scalar matrix (in our case 3×1) and subtracting this number from all the eigenvalues. The eigenvectors are unchanged by this process.

The nature of the numerical method (see Wilkinson 1958) is such that providing the repeated eigenvalue is not exactly the same (in practice $\lambda_i-\lambda_{i-1}>2^{-27}$, about) the two eigenvectors will differ sufficiently for it to be possible to orthogonalize them without great loss of accuracy. However in some cases <u>exactly</u> equal roots are found and it has been found necessary to modify the programme so that in these cases the roots are artificially separated by a suitable small quantity.

When the Secular matrix is such that degeneracies do not occur among the orbitals belonging to any one of the irreducible representations, the method described in the previous section will ensure that correct orthogonal orbitals will be calculated. However it sometimes happens that two or more degenerate orbitals belong to the same irreducible representation. In these cases no one orthonomal set of eigenvectors corresponding to this eigenvalue may be said to be correct and an arbitrary set must be calculated. It is normally safe to assume that the set of vectors produced by the sub-programme will span the appropriate subspace and so an orthonomal set may be derived by the process of orthogonalization. i.e. from the second

vector one subtracts its projection on the first vector and renormalizes. One then subtracts from the third vector its projections on the (now orthogonal) first two vectors, renormalizes, etc.

The library version of Programme - 517 (written by Dr. J.S.Rollett) contains a large number of Mercury machine instructions as the use of these leads to an efficient programme. By even greater use of machine instructions it has been possible to reduce the length of the translated version of the programme sufficiently for an orthogonalization routine to be included in the one Chapter. This version has been used with versions C and D of the HMO Programme.

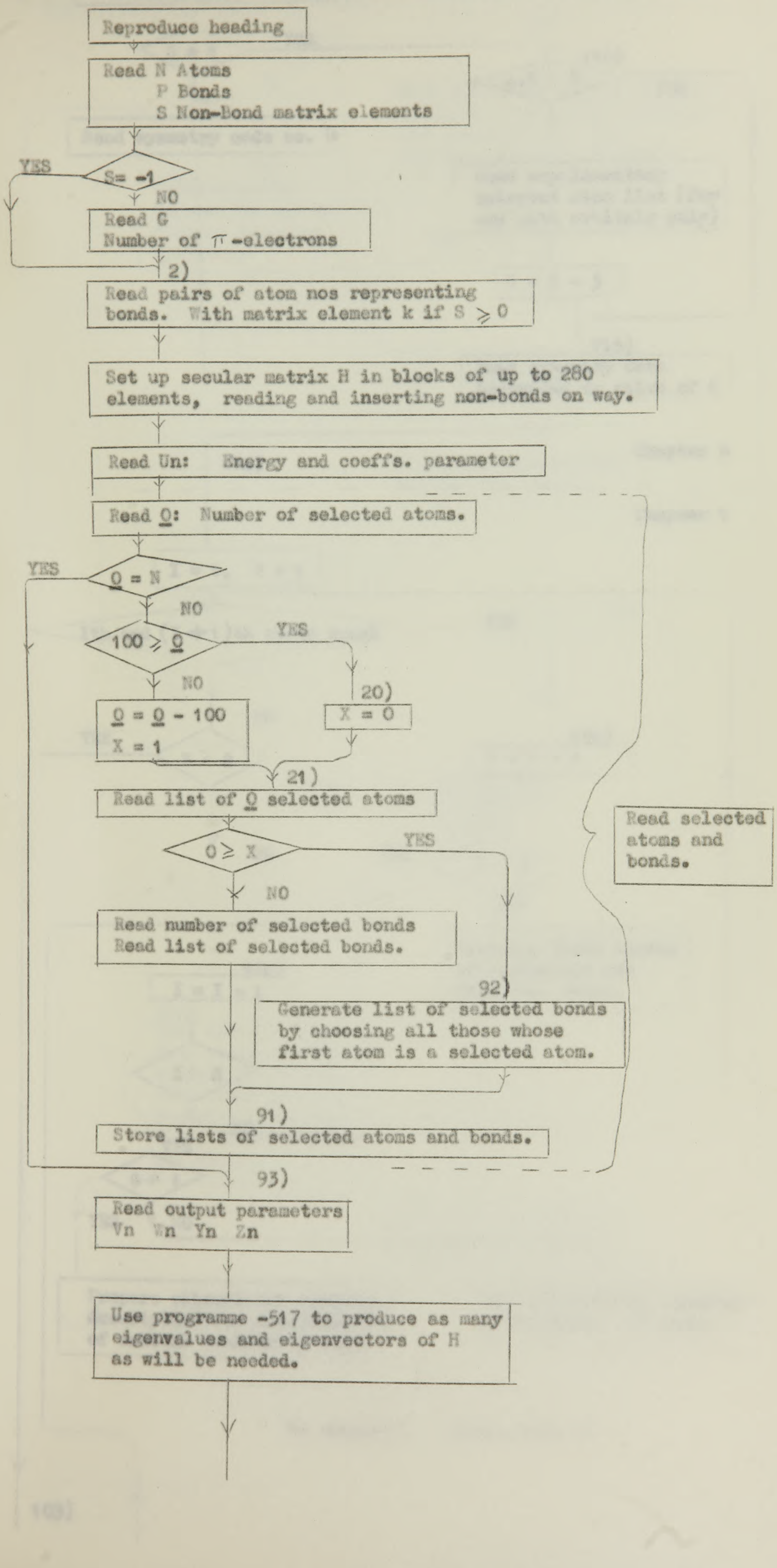
To make it possible for the HMO Programmes to be run on other computers when Mercury is no longer available a version had to be produced in a language acceptable to other computers. (see discoussion of languages below). Suoh a language is the Mercury Autocode language. A version of Programme - 517 in the Autocode Language with no machine instructions has been written by Dr. H.O.Pritchard and others at Manchester University. This programme however has several disadvantages and some actual mistakes which could lead to wrong answers, or to failure in cases where it need not occur. Accordingly a new version of the Programme has been written, following the others in Numerical Method and Logical Structure, but being fully interchangeable with the version mentioned above

which has been used with versions C and D of the HMO Programmes. This version is included in Appendix B to this chapter.

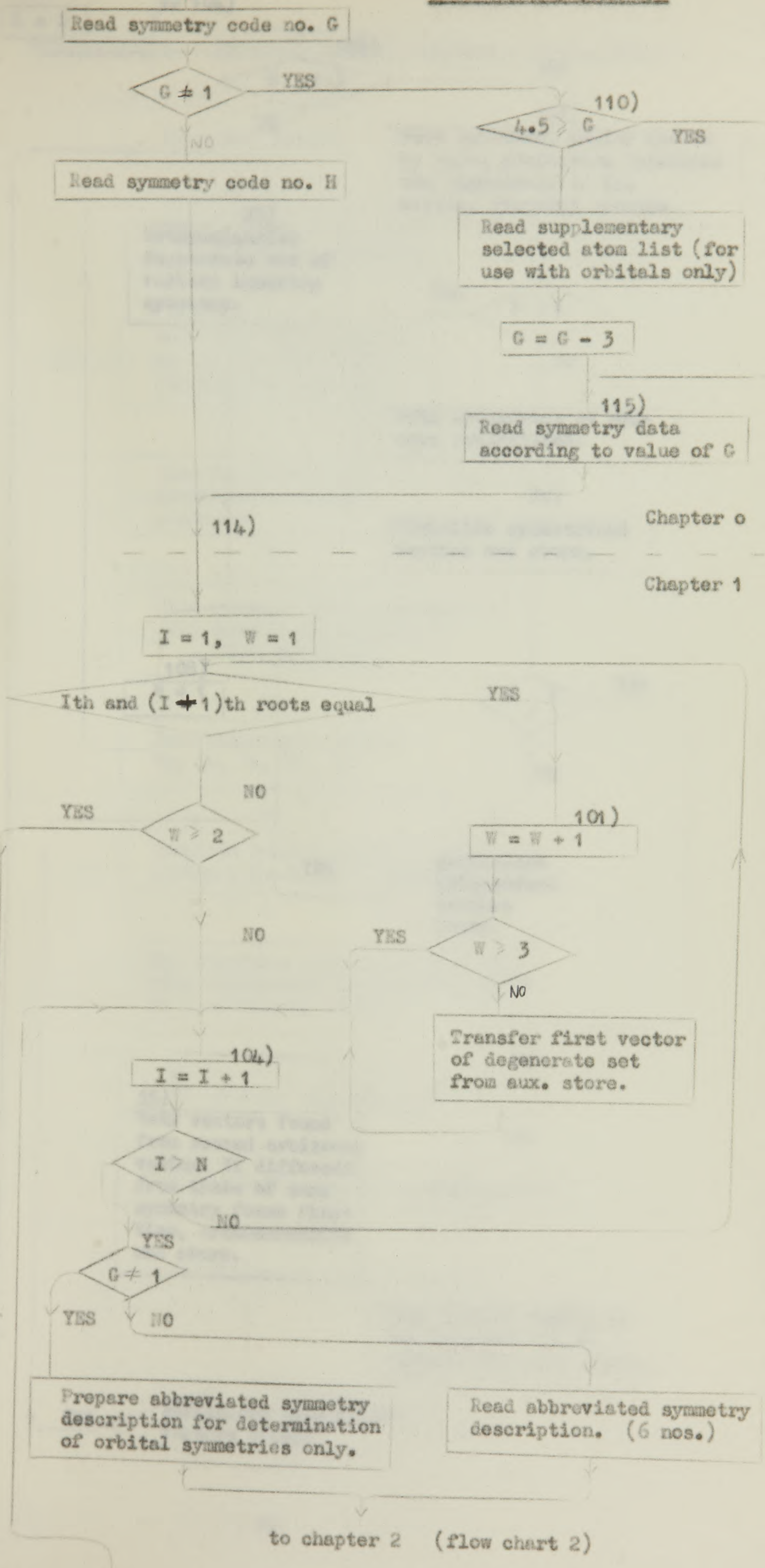
10. Chapters 0 and 1 of the HMO Programmes.

This part of all the versions is concerned with reading in the data, setting up and solving the secular matrices and hence providing the rest of the programme with all necessary eigenvalues, eigenvectors, lists of bonds, lists of selected atoms and bonds, etc. Outline flow diagrams for these chapters are given in the following pages to help in following the programmes themselves given in Appendix B . .. Note that although the five versionsare given separately much of the logical structure and some of the actual programme is common to several versions.

FLOW CHART 3 Logical structure of Chapter 0 version S

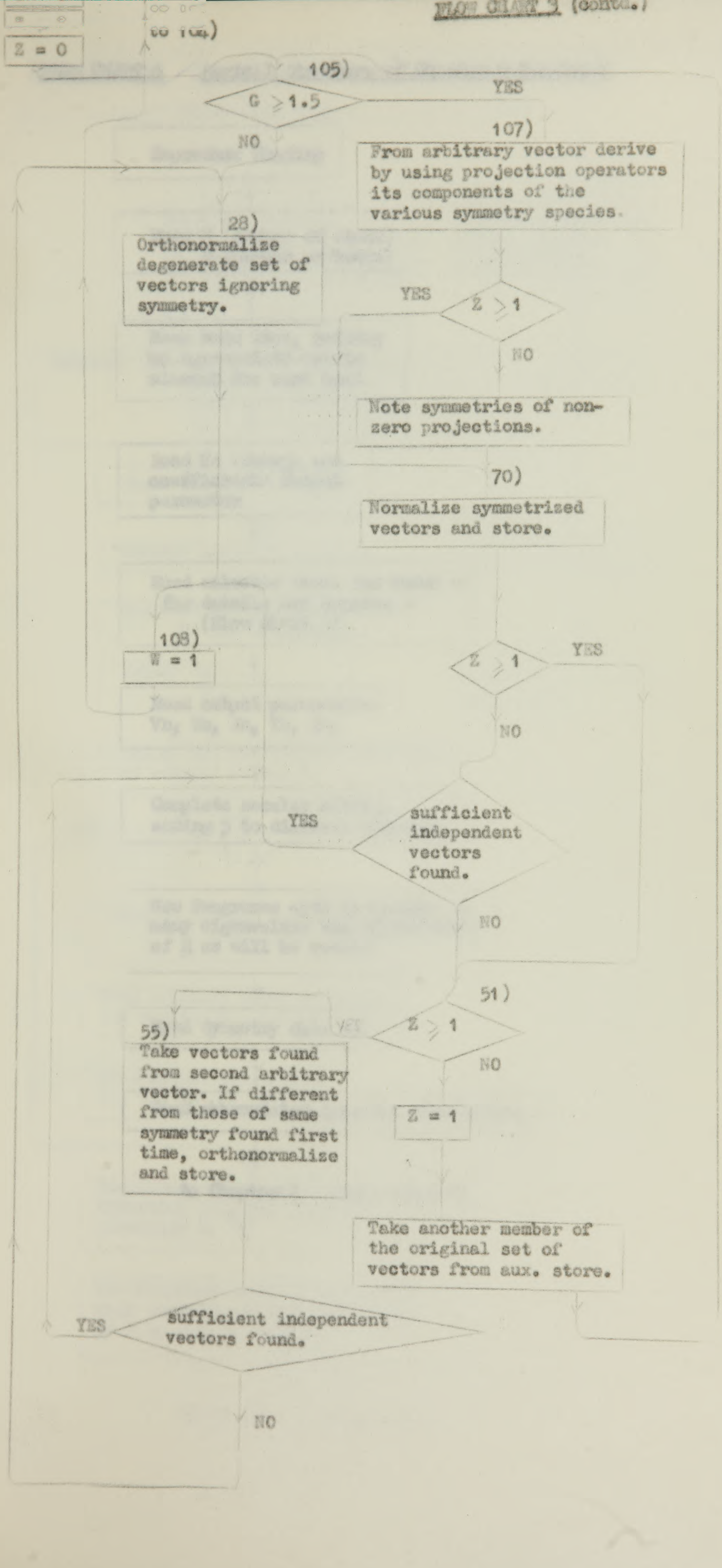


FLOW CHART 3 (contd.)



103)

FLOW CHART 3 (contd.)



FLOW CHART 4 Logical Structure of Chapter 0 Version H

Reproduce Heading

↓

Read N (number of atoms)
R (number of bonds)

↓

Read bond list, setting up appropriate matrix element for each bond

↓

Read Un (Energy and coefficients output parameter

↓

Read selected atoms and bonds - for details see version 5 (Flow chart 3)

↓

Read output parameters:
Vn, Wn, Xn, Yn, Zn,

↓

Complete secular matrix, adding 3 to diagonal elements

↓

Use Programme -517 to produce as many eigenvalues and eigenvectors of H as will be needed

↓

Read Symmetry Code No.

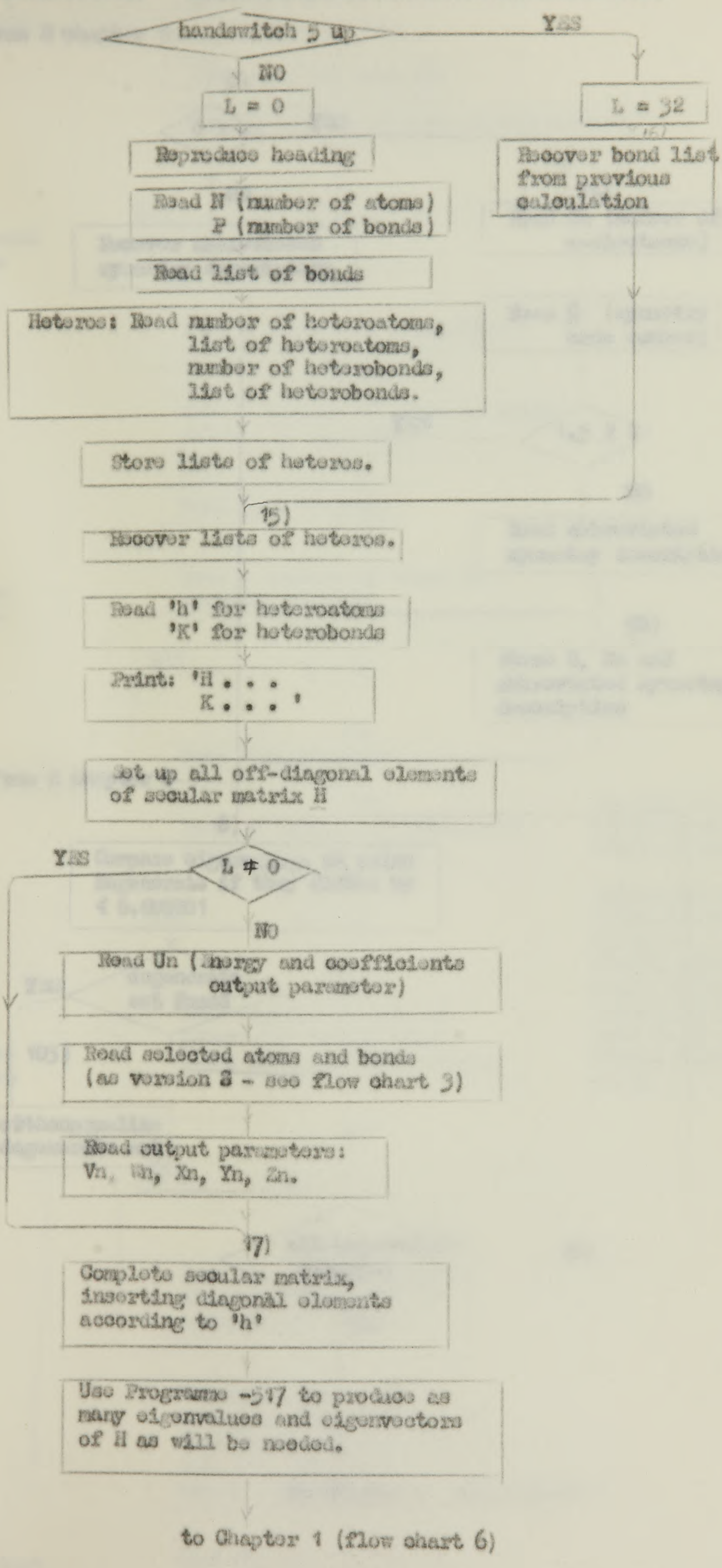
↓

Read abbreviated symmetry description

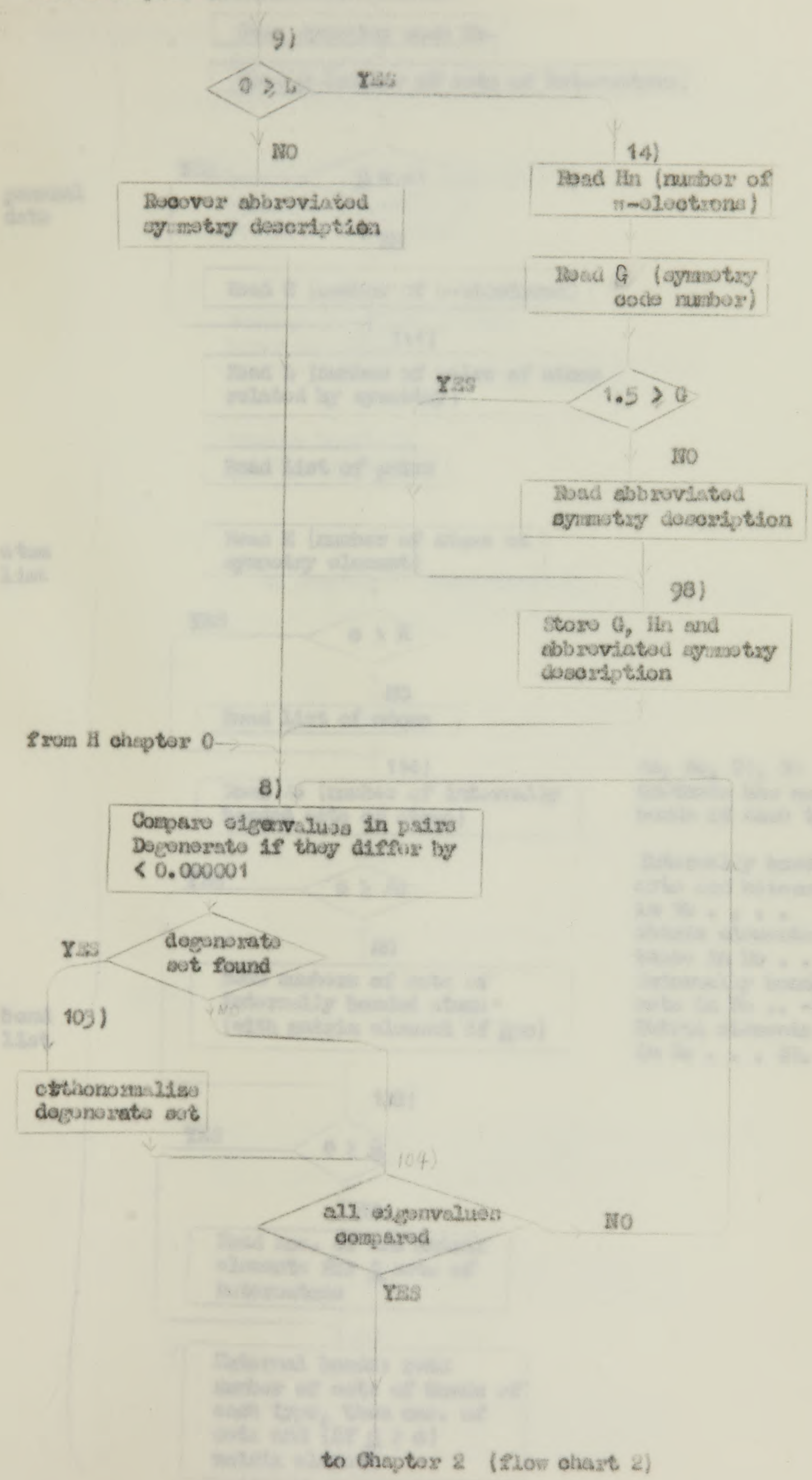
↓

to Chapter 1 (flow chart 6)

FLOW CHART 5 Logical Structure of Chapter 0 Version E



FLOW CHART 6 Logical Structure of Chapter1 Versions H and E



FLOW CHART 7 Logical Structure of Chapter 0 Version C

heading

Reproduce heading

Read symmetry code No.

Read Q (number of sets of heteroatoms)

general data

YES — Q = -1

NO

Read C (number of π-electrons)

111)

Read L (number of pairs of atoms related by symmetry)

Read list of pairs

atom list

Read K (number of atoms on symmetry element)

YES — o > K

NO

Read list of atoms

114)

Ao, Bo, B1, B2 indicate how many bonds of each type

Internally bonded sets and heteros. in Ho . . . .
Matrix elements for these in Do . . . DS.
Externally bonded sets in Fo .. -Ho ..
Matrix elements in Go . . . GR.

Read Ao (number of internally bonded sets of atoms)

bond list

YES — o ≥ Ao

NO

Read numbers of sets of internally bonded atoms (with matrix element if Q>o)

118)

YES — o ≥ Q

NO

Read nos. of and matrix elements for Q sets of heteroatoms

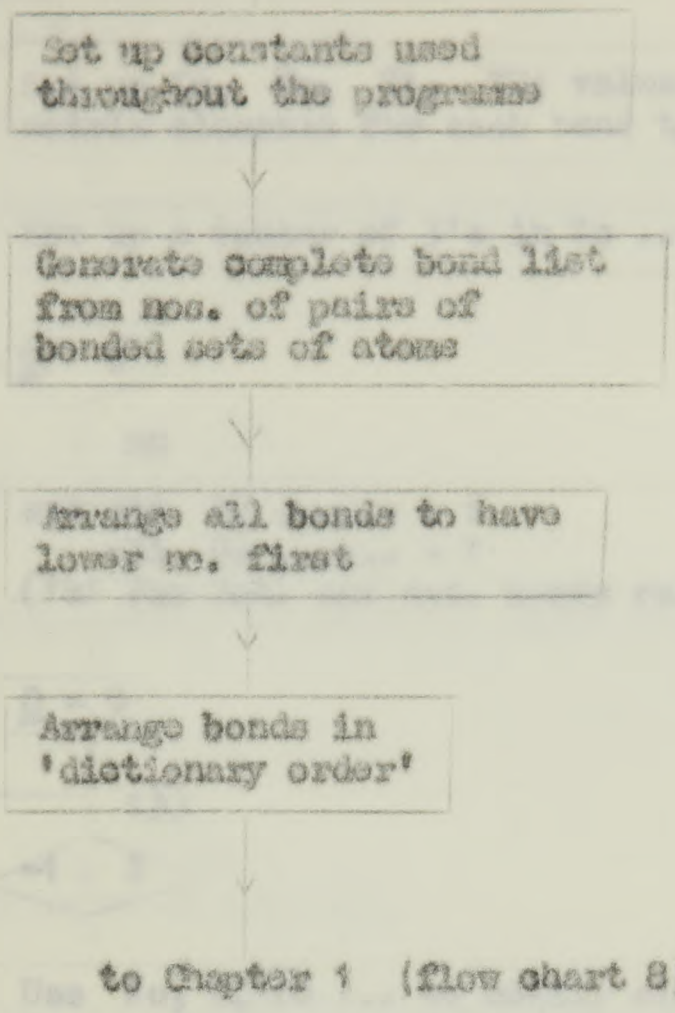
113)

External bonds: read number of sets of bonds of each type, then nos. of sets and (if Q > o) matrix element

output parameters

Read Un, Vn, Wn, Xn, Yn, Zn. (parameters to define output required)

FLOW CHART 7 (continued)



FLOW CHART 8 Logical structure of chapter 1 version C

19)

for S matrix

for A matrix

Set up Xo, Yo, Y1, Y2; values of matrix elements for each bond type in matrix H^i

Set up a vector of 3's in Zo ....

YES — $\underline{O} \neq O$

NO

set all Do ..... = 1
all Go ..... = 1
('k' for int. and ext. bonds respectively)

$\underline{O} = O$

13)

YES — $-1 \geq S$

Use Ao, S, Do ... to modify all diag. elements Zo... if hetero or internally bonded.

14)

Use Bo-B2, Yo-Y2 to set up vectors Eo... (positions of non-zero matrix elements) and Ho... (values of these elements)

from Zo..., Eo..., Ho... set up and store on drum the matrix H^i

Use programme-517 to find roots and vectors of H^i

NO — both matrices done

YES

23)

Take 2 sets of eigenvalues generato an overall list of eigenvalues in descending order. And a list of symmetry types Zo...

Determine no. of eigenvectors needed if polarizabilities wanted = all, otherwise = occupied orbitals only.

Take eigenvectors corresponding to each eigenvalue in turn. From each express vector in terms of atomic orbitals, using atom list.

to chapter 2 (flow chart 2)

FLOW CHART 9 Logical structure of Chpter 0 Version D

heading

Reproduce heading

Read K (number of sets of atoms in general positions)

Read sets of 4 atom nos.

Read L (number of pairs of atoms on z-axis)

YES ← o > L

NO

Read pairs of atom nos.

112)

atom list

Read K (number of pairs of atoms on y-axis)

YES ← o > K

NO

Read pairs of atom nos.

113)

Read L (atom at the origin)

YES ← o > L

NO

Read atom no.

114)

bond list

Internal bonds: Read number of bonds of each type and list of atom-sets

External bonds: Read number of bonds of each type and lists of pairs of atom-sets

generate numbers Ao - A4, Bo - B7 indicating how many bonds of each type. First atom-set of each bond (numbered according to position in atom-list starting at o) put in Fo . . . , second atom set into Ho . . .

output parameters

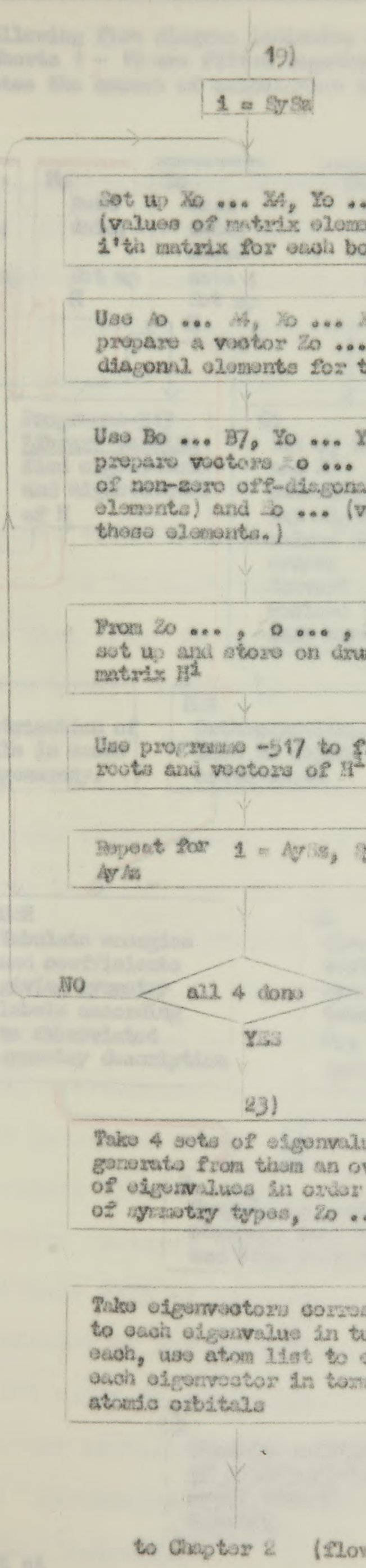
Read Un, Vn, Wn, Xn, Yn, Zn. (parameters to define the calculation and output required)

Set up constants used throughout the rpogramme.

From bond list in terms of atom sets generate complete list of bonds in terms of atom nos.

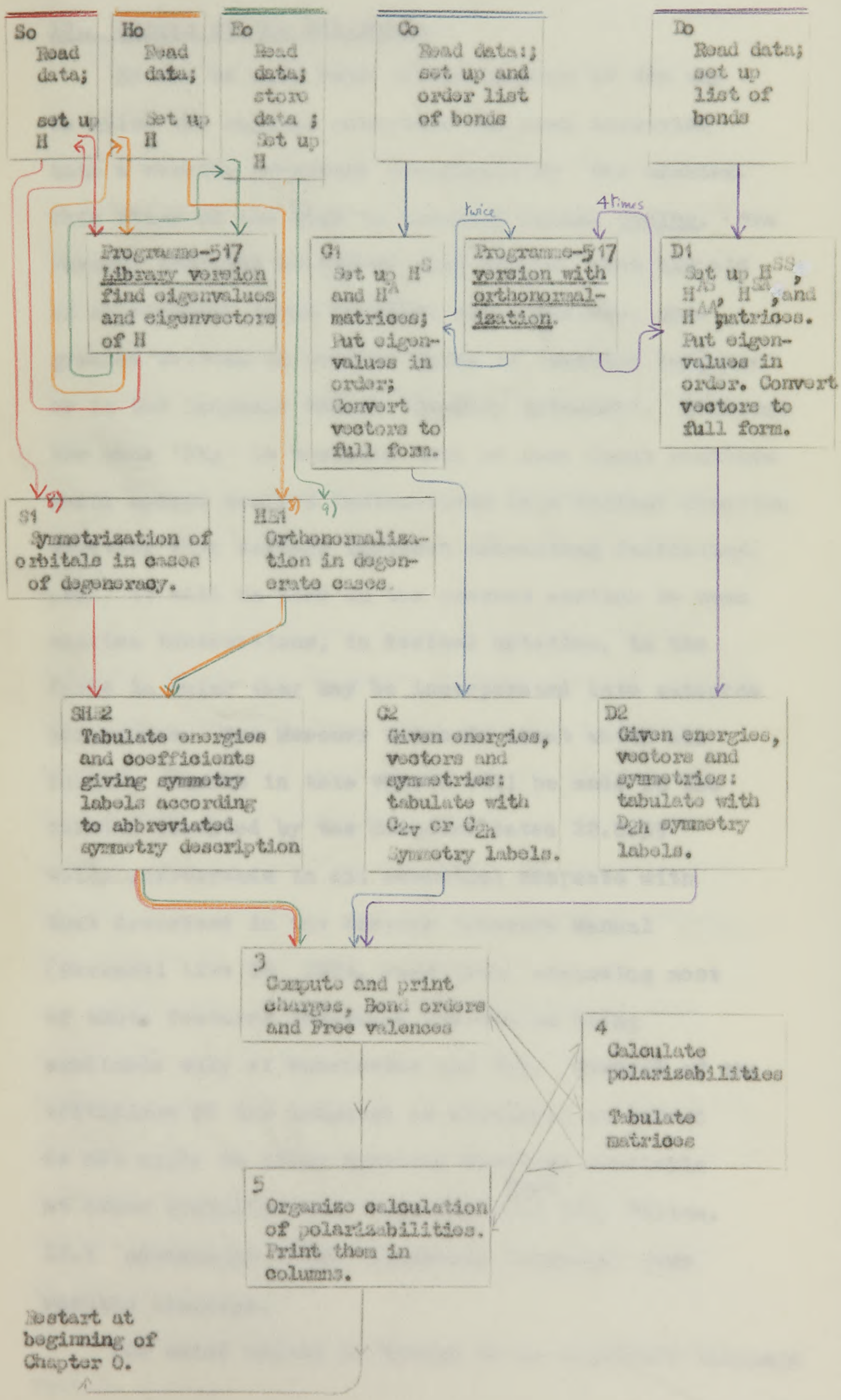
to Chapter 1 (flow chart 10)

FLOW CHART 10 Logical structure of Chapter 1 Version D



11. Composition of the various versions of the programme

The following flow diagram indicates how the chapters described in flow charts 1 - 10 are fitted together into complete programmes and indicates the course of calculation in each version.



12. Coding of the Programme.

So far we have made little mention of the way in which the logical structure has been converted into a working programme acceptable by the machine. This stage of the work is commonly called coding. The Mercury computer at Oxford will accept, with the aid of appropriate input routines and compilers, programmes written in various forms of 'machine language' or in the language called 'Mercury Autocode'. Although the name 'Pig' is strictly that of some input routines which accept machine instructions in a decimal notation together with certain indirect addressing facilities, etc., it will be used in the present section to mean machine instructions, in decimal notation, in the forms in which they may be incorporated into Autocode programmes. The Mercury Autocode about which all further remarks in this thesis will be made is the version accepted by the Compiler dated 22.8.59 which corresponds in all essential respects with that described in the Mercury Autocode Manual (Ferranti list CS 242A, June 1961) excluding most of those features described therein as being available only at Manchester and ICI. Several of the criticisms of the language as available at Oxford do not apply to other improved versions available at other installations, especially that at ICI, Wilton.

12.1 Advantages of an 'algebraic language' over machine language.

The chief points in favour of an algebraic language

like Mercury Autocode may be enumerated as follows:-

1. Similarity to ordinary algebra and hence ease of learning.
2. Relative ease of checking and debugging programmes.
3. Conciseness - and so, on a machine where reading time is of similar order of magnitude to compiling time, a saving of input time.
4. Ability to make use of standard subroutines for e.g. Reading, Printing, Algebraic functions, Matrix operations.
5. Possibility of running the programmes on other computers for which a suitable compiler has been written.

Points 1 and 5 were those which led to the decision to use the Mutocode language for the present work, an added advantage being that the autocode compiler is usually kept in the Oxford machine and that a very simple operating system is used which greatly reduces the need for elaborate communication between the programmer and machine operators during the periods of programme testing.

There are, however, certain features of this particular Autocode which have necessitated, or in certain cases made strongly advisable, the use of the facility for incorporation of Pig instructions into an Autocode programme. Such incorporation of Pig instructions is undesirable as all the above points in favour of an Autocode, except No. 4, no longer hold. If Pig instructions are only incorporated as a last resort, because of facilities not available in Autocode, only the loss of point 5 is serious. It may be possible

on certain machines (e.g; Atlas) to replace Pig instructions by the corresponding machine instructions for the other machine and thereby render the programme usable, but this procedure is not to be rec@ommended.

The shortcomings of Autocode which have led to the use of Pig instructions in the present programmes may be divided into two classes: (i) Particular machine functions which cannot be obtained using the Autocode language. (ii) types of Autocode instructions whose translated versions are greatly longer in storage space and time of execution than they need be.

The Machine instructions, the action of which cannot be simulated using Autocode, are chiefly among those which operate on integers and half-registers - especially; reading of a single tape character into, and punching a character from, a half register; the use of relative addressing (B-modification) in half-registers; the logical operations & and ≠ and the halving function; the extraction of the exponent of the accumulator into a B-register, etc. and the reading of an integer from the handswitches.

The most common type of autocode programme which is inefficiently translated is one where an index is used repeatedly as a suffix in a group of instructions. The autocode compiler causes a fresh copy of the index to be taken into a B-register each time it is used, whereas an efficient programme would need only to do this once.

Another limitation of the Autocode system which often leads to the use of Pig instructions is the limitation to 12 half-registers for use as indices.

Very often one wants to consider large numbers of small integers which would waste valuable space if put into a long register each.

Pig instructions are also useful for taking advantage of certain features of standard Autocode functions. e.g. one may wish to calculate the reciprocal of the square-root of a number. The method used to calculate square-root in fact gives the reciprocal which is then multiplied by the original argument to give its square root. The reciprocal remains in a particular register of the computer after this operation and may be extracted by a suitable Pig instruction. One may wish to print a number on the output tape without the standard termination of two spaces - this can only be done by using Pig instructions.

During the development stages large parts of the HMO programmes were written in Pig, often to save chapter space, but sometimes for stronger reasons as described above. In order that the Programmes may be available for other computers most versions have now been rewritten using as little Pig as possible and these are the versions which are given in Appendix B. These are probably slightlyslower in operation than some of the earlier versions but not significantly so. No exact timing comparisons have been carried out.

13. Experience with the HMO Programmes.

The chief use which has been made of the programmes to date has been for the Dictionary of π-electron calculations. Some other original calculations have been done both by myself and by other people in Oxford

Some of the results of these are given and are discussed below(section 14). The development of the programmes was spread over about a year, and several minor mistakes have been corrected since the working versions were first run. All versions except D are now in a form which can easily be converted for use on other computers which will accept the Auto code language. If version D is required for use on other computers it is re-commended that it be modified to accept Heterosystems.

13.1 Accuracy of the results.

As such a large quantity of Huckel calculations have been done and results published in the literature, the development of the programme was greatly eased as a large variety of known results could be reproduced. The numerical methods involved being essentially straighforward, the mistakes made in writing the programme were chiefly connected with programming logic; many of these would have been avoided if logical flow diagrams as included in this thesis had been prepared before attempting to write the programmes. Many other troubles which occurred during development can be attributed to my lack of programming experience at the time of writing the programme.*

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* I consider that the Oxford computer would be much more efficiently used if a follow-up course in programming methods were given which all users would be expected to attend after a few months experience of writing programmes. I do not consider that the

The Huckel theory itself provides many checks which may be applied to the calculated quantities. Many of these are given by Coulson and Longuet-Higgins (1947 a,b ,1948) and have been used to check manually some of the computed quantities. In no cases have these checks been found to fail to within the accuracy of the 5-decimal tabulated answers. Errors due to mistakes in the data are reduced to a minimum by having forms on which the data may be prepared and checked. Errors which are not detected at this stage often cause failure of the programme to read the data at all, or sometimes give gross errors like all eigenvalues zero, negative free-valences and others which are easy to spot. The few query-prints (Autocode Manual p.9) which are included in the programmes are often useful for tracing the cause of such errors. Consequently , unless the calculation has been done before, it is recommended that queries are not suppressed, there being so few that the time spent punching them is not great. The output proper is preceded by 3" blank tape and so the

- -

existing introductory course should be extended as, at that stage, one does not know what is going to be of importance to one's particular problem, but feel that a second course a few months later would eliminate much superfluous testing and reduce the number of inefficient programmes being used for long production runs.

query prints may easily be omitted on the teleprinter.

13.2 Time taken for the computations.

An accurate assessment of the time taken by various parts of the programme has not been made. The parts of the programme which take longest are the diagonalization of the secular matrix and the calculation of complete matrices of polarizabilities. The time taken by the former is proportional to n^3 (or to $\sum n_i^3$ if version C or D is used to set up matrices i for the different irreducible representations). The latter takes a time proportional to n^a where $2<a<3$. For large calculations the time taken actually punching out the tables becomes considerable.

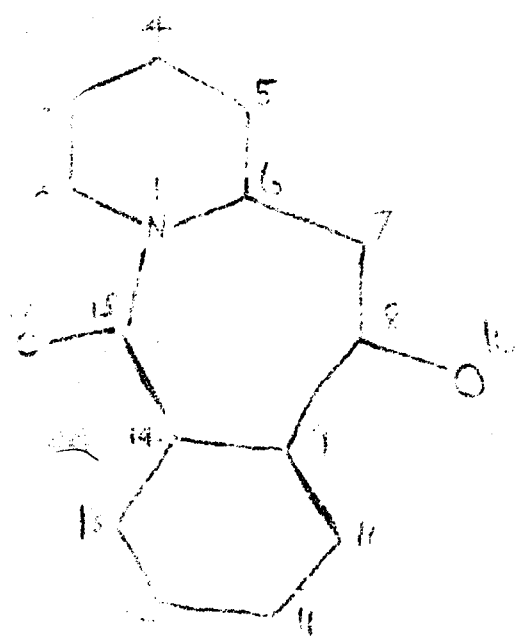
The largest complete HMO calculation (printing all polarizabilities but using the two-fold symmetry as much as possible) which was done for the Dictionary of π-electron calculations took about 10 minutes. This was for the molecule fluoranthene with 16 π-centres. The largest molecule treated so far by any version had 44 π-electrons and took 11 minutes to compute (with version C) and tabulate the energies and coefficients, bond orders, free valences and the atom-atom self-polarizabilities only.

14. Discussion of results for some particular molecules

14.1 Thyagarajan's molecule.

HMO Programme S was used for a complete calculation for the molecule indicated in Fig. 14.1 below, the synthesis of which has been attempted by Dr. B.S.Thyagarajan of the University of Madras.

Fig. 14.1



This system has 18 π-electrons, one from each of the 17 centres plus a second one from the nitrogen atom. The values used for the atom and bond parameters were those suggested by Streitwieser (1961, p.135) for pyrrole-like nitrogen, and oxygen with a single π-electron. These are:

$$h_N = 1.5$$

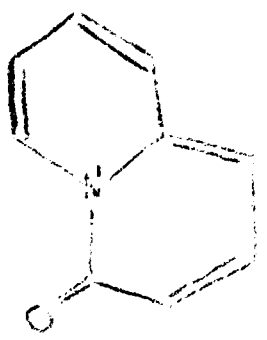
$$h_O = 1.0$$

$$k_{CN} = 0.8$$

$$k_{CO} = 1.0$$

The results of the complete calculation are given in the accompanying table, which was the result of about 15 minutes computing time.

Thyagarajan (1962) has observed that his molecule resembles in many respects (spectra in acid and alkaline ethanol etc.) the molecule 4 -ketoquinolizine.

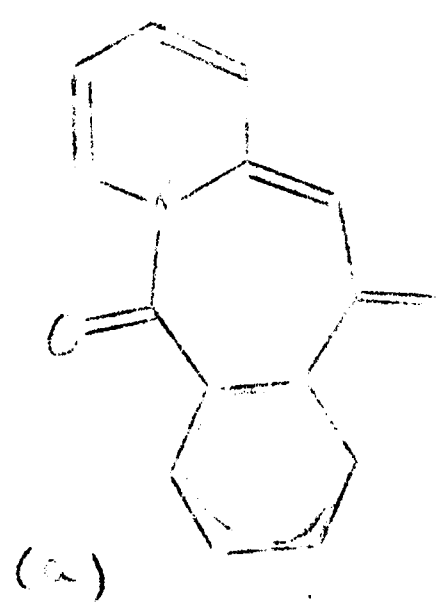


The near equality of the calculated bond orders for the ring 9-10-11-12-13-14 and the low values of the orders of bonds 8-9 and 14-15 imply that this ring is trulybenzenoid and hence relatively unreactive. This is consistent with the observed independence of the rest of the molecule of the presence of this ring.

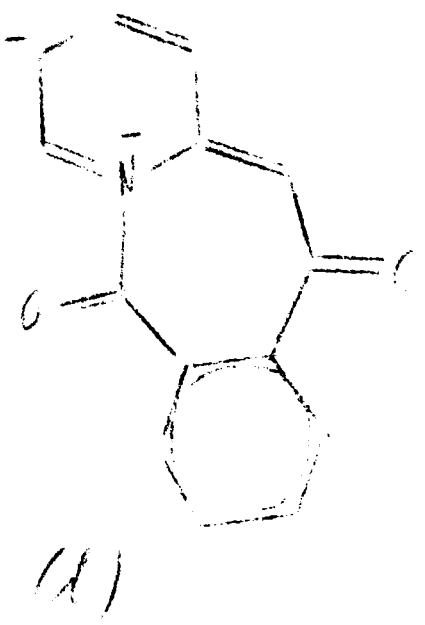
Thyagarajan correlates the IR absorption maxima at 1653 cm^{-1} and 1638 cm^{-1} with the stretching of the -c=O bonds 15-17 and 8-16 respectively (the single maximum in this region in the spectrum of 4-ketoquinolisine is at 1658 cm^{-1}). The different maxima agree qualitatively with the calculated bond orders for these bonds -an accurate correlation should not be expected because of the difficulty of correct parameter choice. (See e.g. Streitwieser 1961 Chap.8).

The calculated distribution of bond orders and charges may be compared with the Kekulé structures that may be drawn for the molecule.

The only unexited Kekulé structure (assuming the lower ring as perfectly benzenoid) is (a)



(a)



(d)

THYAGARAJAN 2

ENERGY

	S=0
I	2.671740
2	2.228220
3	I.260887
4	I.651II4
5	I.357842
6	I.20I752
7	I.000000
8	I.000000
9	0.45I575
I0	-0.307481
II	-0.423828
I2	-0.819404
I3	-I.I47325
I4	-I.395944
I5	-I.572712
I6	-I.983074
I7	-2.285488

TOTAL PI ENERGY
27.052463

COEFFICIENTS

	I	2	3	4	5	6
E	2.67474	2.22822	I.2608	I.65II4	I.3578	I.20I75
I	0.62I64	-0.37892	0.02507	-0.05206	-0.45795	0.I5I44
2	0.23315	-0.I2874	-0.04742	0.I4893	-0.00235	0.44I77
3	0.I27I0	-0.I2071	-0.II304	0.28755	0.36317	0.40974
4	0.I065I	-0.II258	-0.I7423	0.32586	0.49548	0.25064
5	0.I5779	-0.IIII6	-0.22862	0.25049	0.30961	-0.34889
6	0.3I554	-0.I3511	-0.27406	0.08773	-0.07507	-0.46991
7	0.I8888	0.II323	-0.32883	-0.06398	-0.04518	-0.33698
8	0.I8966	0.38742	-0.37075	-0.I9338	0.0I372	0.06495
9	0.20517	0.43464	-0.0I232	0.04I67	0.02548	0.09310
I0	0.I0049	0.29367	0.05753	0.24897	-0.II734	0.06I77
II	0.06362	0.2I973	0.I2513	0.36942	-0.I848I	-0.0I887
I2	0.06967	0.I9596	0.I8784	0.36099	-0.I3360	-0.08445
I3	0.I2274	0.2I693	0.24320	0.22663	0.00340	-0.08261
I4	0.25863	0.28742	0.28905	0.0I32I	0.I2822	-0.0I483
I5	0.30385	-0.0III1	-0.33592	-0.24859	0.I5889	-0.02831
I6	0.II325	0.3I54I	-0.38584	-0.23698	0.05833	0.32I93
I7	0.2I726	-0.00904	0.34950	-0.37856	0.44377	-0.I4034

	7	8	9	I0	II	I2
E	I.00000	I.00000	0.4515	-0.3074	-0.4238	-0.8I94
I	0.00000	0.00000	-0.I827I	-0.I6227	0.27743	0.I8I27
2	-0.00000	-0.00000	0.32240	0.42071	-0.09341	-0.38868
3	-0.00000	-0.00000	0.20I75	-0.03729	-0.I8235	0.I7348
4	-0.00000	-0.00000	-0.I9065	-0.40559	0.I7070	0.24654
5	0.00000	-0.00000	-0.37785	0.I9851	0.II001	-0.37549
6	0.00000	-0.00000	0.02003	0.32669	-0.2I732	0.06II4
7	-0.00000	-0.00000	0.53306	-0.I9855	-0.23984	0.I8038
8	-0.00000	-0.00000	0.22069	-0.24777	0.3I897	-0.20894
9	0.48366	-0.06453	-0.03I00	0.II973	0.32867	-0.I2401
I0	0.33I06	-0.48200	-0.I4655	0.I8559	-0.I3707	0.40216
II	-0.25261	-0.4I747	-0.03518	-0.I9350	-0.27058	-0.20552
I2	-0.48366	0.06453	0.I3066	-0.I0867	0.25I75	-0.23375
I3	-0.33I06	0.48200	0.0941I	0.23669	0.I6338	0.39706
I4	0.25261	0.4I747	-0.08813	0.0I459	-0.32I2I	-0.09I60
I5	0.00000	0.00000	-0.I0299	-0.36223	-0.35642	-0.I9799
I6	-0.48366	0.06453	-0.40240	0.I7730	-0.22402	0.II484
I7	-0.25261	-0.4I747	0.I8779	0.25920	0.25033	0.I0882

	13	14	15	16	17
E	-1.11740	-1.09591	-1.57271	-1.03007	-2.23549
1	0.00118	0.10882	-0.02082	0.20905	-0.03170
2	-0.34760	0.00633	0.26107	-0.23700	0.00710
3	0.39536	-0.11005	-0.09535	0.09356	0.00915
4	-0.10524	0.16111	0.05980	-0.06105	-0.02805
5	-0.27380	-0.10105	-0.17051	0.42049	0.05491
6	0.12010	-0.01160	-0.00164	-0.16030	-0.00747
7	-0.21180	0.01422	0.33129	0.34334	0.10330
8	-0.17708	-0.00536	-0.42038	-0.21187	-0.54439
9	0.33253	-0.00908	0.17711	0.00601	0.48991
10	-0.26034	-0.35486	0.02720	0.03111	-0.32128
11	-0.03081	0.50444	-0.21988	-0.06773	0.24548
12	0.39913	-0.31032	0.31861	0.10327	-0.33976
13	-0.30041	-0.01683	-0.28121	-0.13715	0.30249
14	0.05588	0.37270	0.12364	0.16884	-0.45153
15	-0.08733	-0.49150	-0.09036	-0.20383	0.24078
16	0.08246	0.00219	0.16690	0.07100	0.10479
17	0.04062	0.20639	0.03512	0.06831	-0.07329

BOND ORDERS

1	2	0.44111
1	6	0.39093
1	15	0.38690
2	3	0.75968
3	4	0.57546
4	5	0.71711
5	6	0.56514
6	7	0.60244
7	8	0.61823
8	9	0.40674
8	16	0.55357
9	10	0.61617
9	14	0.55018
10	11	0.67726
11	12	0.64256
12	13	0.68049
13	14	0.60728
14	15	0.43239
15	17	0.69000

CHARGES

1	1.59878
2	0.83506
3	1.03207
4	0.88994
5	1.02523
6	0.85405
7	1.12093
8	0.82805
9	0.96254
10	0.97283
11	0.95661
12	0.97801
13	0.94811
14	0.99683
15	0.68547
16	1.70901
17	1.60559

FREE VALENCES

1	0.51311
2	0.53126
3	0.39692
4	0.43948
5	0.44980
6	0.17353
7	0.51139
8	0.15353
9	0.15896
10	0.43862
11	0.41223
12	0.40900
13	0.44428
14	0.14220
15	0.22276
16	1.17849
17	1.04205

POLARIZABILITIES

ATOM-ATOM

	1	2	3	4	5	6
1	-0.23861					
2	0.04085	-0.50505				
3	-0.00125	0.23916	-0.40259			
4	0.02633	-0.01718	0.09281	-0.42128		
5	0.00090	0.13405	-0.02193	0.21150	-0.44586	
6	0.03417	0.02516	0.03247	0.00259	0.09085	-0.35758
7	0.00215	0.02984	-0.00695	0.04493	-0.03560	0.11642
8	0.02196	0.02491	0.01776	0.02088	0.02383	0.00825
9	0.00214	0.00009	0.00098	0.00066	0.00001	0.00265
10	0.00582	0.00518	0.00409	0.00464	0.00493	0.00316
11	0.00418	-0.00053	0.00189	0.00003	0.00143	0.00048
12	0.00391	0.00614	0.00348	0.00537	0.00424	0.00442
13	0.00673	-0.00206	0.00237	-0.00095	0.00169	-0.00053
14	-0.00088	0.00870	0.00300	0.00679	0.00436	0.00545
15	0.03772	-0.00873	0.01002	-0.00298	0.00704	-0.00191
16	0.02550	0.02437	0.01431	0.02669	0.01065	0.03316
17	0.02709	-0.00479	0.01036	-0.00083	0.00792	0.00078

	7	8	9	10	11	12
7	-0.48901					
8	0.13701	-0.33889				
9	-0.00434	0.03101	-0.36174			
10	0.02335	-0.00922	0.13004	-0.42667		
11	0.00655	0.00228	-0.00877	0.16551	-0.40957	
12	0.01848	-0.00184	0.07532	-0.01558	0.13930	-0.42653
13	0.00861	0.00036	0.09659	-0.01337	-0.09352	0.16793
14	0.01838	-0.00489	0.09730	-0.00083	0.07326	-0.01065
15	0.03603	0.00342	0.00801	0.00061	0.01122	0.00242
16	0.05229	0.00615	-0.00491	0.00835	-0.00000	0.00706
17	0.04117	0.00132	0.02873	-0.00031	0.02615	-0.00065

	13	14	15	16	17
13	-0.42854				
14	0.12402	-0.35483			
15	0.00316	0.03417	-0.30964		
16	0.00014	0.00812	0.00132	-0.26897	
17	0.03012	-0.01140	0.16812	0.00024	-0.32428

BOND-BOND

	1- 2	1- 6	1-15	2- 3	3- 4	4- 5
1- 2	-0.38692					
1- 6	0.00531	-0.33670				
1-15	0.07058	0.05974	-0.33033			
2- 3	0.19014	-0.02456	-0.02703	-0.22842		
3- 4	-0.12306	0.00851	0.02265	0.02818	-0.53691	
4- 5	0.07140	-0.04900	-0.01264	-0.12760	0.21475	-0.24119
5- 6	-0.07844	0.07521	0.01178	0.07693	0.11049	0.21469
6- 7	0.05908	0.13564	-0.03997	-0.04821	0.06766	-0.09476
7- 8	-0.04013	0.07780	0.03397	0.03785	-0.04783	0.05729
8- 9	-0.00815	0.00257	-0.01369	-0.00515	-0.02061	0.00028
8-16	0.05049	0.03333	-0.01764	0.04121	0.04361	-0.05152
9-10	-0.33051					
9-14	-0.26175					
10-11	-0.10032	-0.25300				
11-12	0.06400	0.21044	-0.27072			
12-13	-0.09783	-0.12330	0.02187	-0.25139		
13-14	0.13512	0.07550	-0.11800	0.19642	-0.26586	
14-15	0.10368	0.01087	0.02055	-0.03038	0.11773	-0.34625
15-17	-0.04837	-0.00009	-0.01768	0.02135	-0.05450	0.16665

	9-14	10-11	11-12	12-13	13-14	14-15
9-14	-0.26175					
10-11	-0.10032	-0.25300				
11-12	0.06400	0.21044	-0.27072			
12-13	-0.09783	-0.12330	0.02187	-0.25139		
13-14	0.13512	0.07550	-0.11800	0.19642	-0.26586	
14-15	0.10368	0.01087	0.02055	-0.03038	0.11773	-0.34625
15-17	-0.04837	-0.00009	-0.01768	0.02135	-0.05450	0.16665

	5- 6	6- 7	7- 8	8- 9	8-16	9-10
5- 6	-0.33051					
6- 7	0.19580	-0.35172				
7- 8	-0.09023	0.23426	-0.32637			
8- 9	0.00567	0.08895	-0.08539	-0.32689		
8-16	0.06541	-0.13350	0.22756	0.11211	-0.43046	
9-10	-0.00180	0.00540	-0.02205	0.10473	-0.05379	-0.25628
9-14	-0.00101	0.00318	-0.01949	0.09262	-0.02949	0.14120
10-11	-0.00037	0.00083	0.00449	-0.02699	0.01293	0.22015
11-12	0.00085	-0.00218	-0.00224	0.01777	-0.01032	-0.11836
12-13	-0.00221	0.00608	-0.00637	0.00796	0.00039	0.07755
12-15	0.00229	-0.00766	0.00736	-0.00163	0.00010	-0.00918
13-14	0.00255	-0.00176	0.00166	-0.00178	0.00026	-0.00151
14-15	-0.00534	0.01309	-0.02222	0.02172	-0.00265	0.00116
15-17	-0.00536	0.01309	-0.02222	0.02172	-0.00265	0.00116

	5- 6	6- 7	7- 8	8- 9	8-16	9-10
5- 6	-0.33051					
6- 7	0.19580	-0.35172				
7- 8	-0.09023	0.23426	-0.32637			
8- 9	0.00567	0.08895	-0.08539	-0.32689		
8-16	0.06541	-0.13350	0.22756	0.11211	-0.43046	
9-10	-0.00180	0.00540	-0.02205	0.10473	-0.05379	-0.25628
9-14	-0.00101	0.00318	-0.01949	0.09262	-0.02949	0.14120
10-11	-0.00037	0.00083	0.00449	-0.02699	0.01293	0.22015
11-12	0.00085	-0.00218	-0.00224	0.01777	-0.01032	-0.11836
12-13	-0.00221	0.00608	-0.00637	0.00796	0.00039	0.07755
12-15	0.00229	-0.00766	0.00736	-0.00163	0.00010	-0.00918
13-14	0.00255	-0.00176	0.00166	-0.00178	0.00026	-0.00151
14-15	-0.00534	0.01309	-0.02222	0.02172	-0.00265	0.00116
15-17	-0.00536	0.01309	-0.02222	0.02172	-0.00265	0.00116

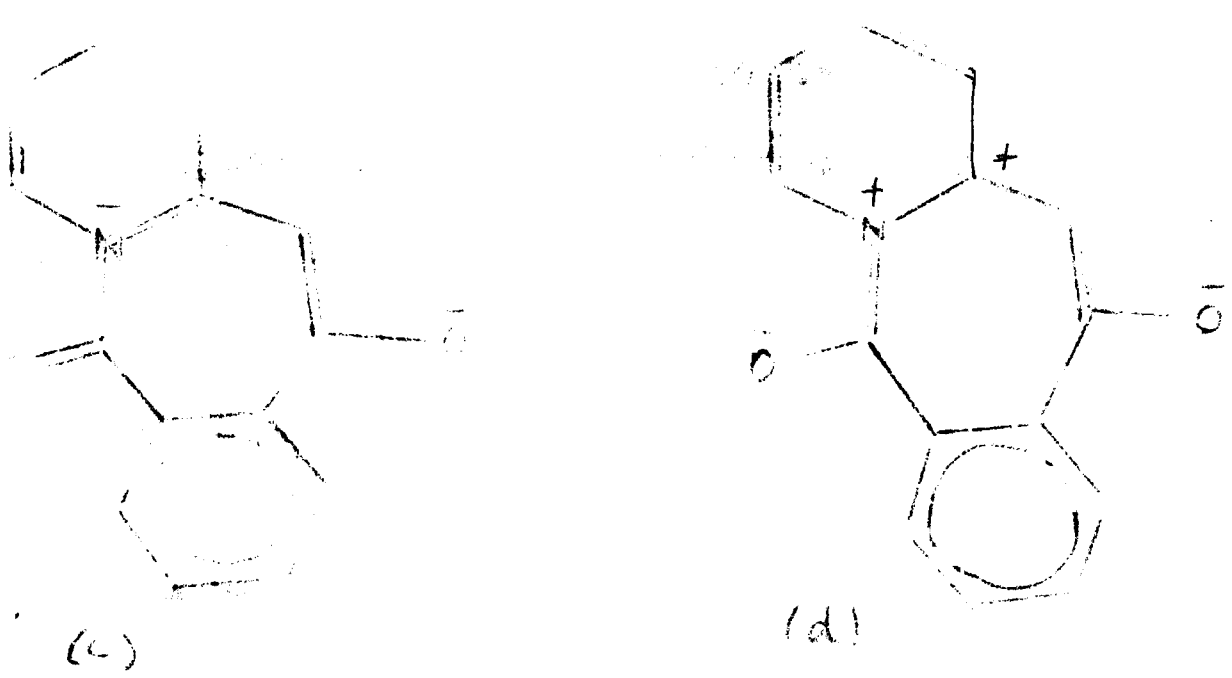
ATOM-BOND

	1	2	3	4	5	6
1- 2	0.22483	0.08958	-0.06538	-0.01965	-0.02043	-0.05764
1- 6	0.18555	-0.06202	0.03083	-0.02934	0.00357	0.03586
1-15	0.15789	-0.03100	0.01849	-0.00525	0.00760	-0.00382
2- 3	-0.06007	-0.20683	0.00718	0.06077	0.02448	0.05683
3- 4	0.04348	0.16171	0.03442	-0.04346	-0.02520	-0.04673
4- 5	-0.00788	-0.11667	-0.01712	-0.11451	0.03833	0.07652
5- 6	0.00316	0.12481	0.01640	0.12764	-0.00444	-0.09493
6- 7	-0.06956	-0.06447	-0.03096	-0.07438	-0.01683	-0.10382
7- 8	0.04627	0.05831	0.02076	0.06812	0.00593	0.09495
8- 9	0.01567	-0.00407	0.01266	-0.00752	0.01788	-0.01613
8-16	-0.05007	-0.05045	-0.03292	-0.04966	-0.03376	-0.04791
9-10	-0.00944	0.00211	-0.00659	0.00334	-0.00862	0.00661
9-14	-0.00106	0.00180	-0.00414	0.00430	-0.00702	0.00883
10-11	0.01017	-0.00145	0.00620	-0.00161	0.00676	-0.00259
11-12	-0.00771	0.00136	-0.00536	0.00184	-0.00605	0.00289
12-13	0.00964	-0.00049	0.00573	0.00002	0.00511	0.00101
13-14	-0.00724	-0.00025	-0.00552	-0.00036	-0.00493	-0.00170
14-15	0.00649	0.00101	0.01069	-0.00084	0.01113	0.00015
15-17	-0.07111	0.01554	-0.02138	0.00433	-0.01527	0.00131

	7	8	9	10	11	12
1- 2	-0.02938	-0.04795	0.00022	-0.01067	0.00011	-0.01047
1- 6	-0.07064	-0.03818	0.00679	-0.01101	0.00282	-0.00829
1-15	0.05798	0.01863	-0.00857	0.00074	-0.01556	0.00648
2- 3	0.01735	0.04216	-0.00033	0.00919	-0.00018	0.00925
3- 4	-0.02755	-0.04167	0.00226	-0.00958	0.00102	-0.00883
4- 5	0.02130	0.05261	-0.00215	0.01130	-0.00080	0.01074
5- 6	-0.03219	-0.06257	0.00439	-0.01316	0.00150	-0.01169
6- 7	0.07983	0.12402	-0.01052	0.02599	-0.00345	0.02222
7- 8	0.05892	-0.16170	0.02746	-0.03340	0.00825	-0.02325
8- 9	0.07035	-0.06777	-0.03455	0.05026	-0.00792	0.03789
8-16	-0.17596	0.04343	-0.01319	-0.00241	-0.00195	-0.00624
9-10	-0.03826	0.02496	-0.02905	-0.01663	0.04189	-0.01537
9-14	-0.02415	0.02253	-0.00699	-0.02695	-0.02817	-0.01202
10-11	0.03085	-0.01052	0.03572	-0.02487	-0.04142	0.02017
11-12	-0.02605	0.00890	-0.02994	0.02533	-0.03087	-0.01269
12-13	0.02503	-0.00050	0.04044	-0.02054	0.03835	-0.02492
13-14	-0.02469	0.00008	-0.04194	0.02660	-0.02975	0.02048
14-15	0.05241	-0.01110	0.07461	-0.00141	0.07139	-0.00699
15-17	-0.08119	-0.00466	-0.04207	-0.00016	-0.04019	-0.00116

	13	14	15	16	17
1- 2	-0.00027	-0.00913	-0.01345	-0.04956	0.01924
1- 6	0.00004	-0.00353	0.00003	-0.05077	0.01729
1-15	-0.02201	0.01371	-0.05090	0.01487	-0.15928
2- 3	-0.00052	0.00988	0.00252	0.03774	-0.00942
3- 4	0.00072	-0.00885	0.00158	-0.04204	0.00877
4- 5	-0.00103	0.01198	-0.00229	0.04576	-0.00610
5- 6	0.00120	-0.01280	0.00423	-0.05822	0.00667
6- 7	-0.00193	0.02288	-0.00586	0.12445	-0.01762
7- 8	0.00227	-0.01930	0.02347	-0.19582	0.01877
8- 9	-0.00206	0.03655	-0.01967	-0.07104	-0.01952
8-16	-0.00063	-0.00575	-0.00466	0.43340	-0.00127
9-10	0.04526	-0.02578	-0.00205	0.02581	0.00181
9-14	-0.04470	0.01491	0.04740	0.02222	0.03321
10-11	-0.03920	0.02403	0.00108	-0.01111	-0.00221
11-12	0.04780	-0.01056	0.01767	0.00916	0.01432
12-13	-0.05223	0.01204	-0.02063	-0.00127	-0.01678
13-14	-0.02570	0.00519	0.05120	0.00092	0.03758
14-15	0.08763	-0.04546	-0.13829	-0.01264	-0.09877
15-17	-0.03915	-0.00518	-0.13025	-0.00127	0.43218

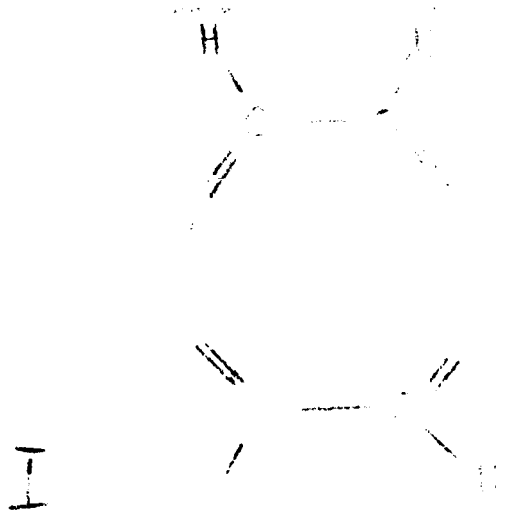
All bonds marked as double in this structure have order > .6 (except the C-O bond 8-16). The most stable singly excited structures will be those with the positive charge on the nitrogen as in (b) and (c), other positions for the negative charge are 5,7 and 17. These positions are those with greatest calculated negative charge. The only doubly excited structures of importance will be those with the two negative charges on the oxygens as in (d). The second positive charge may be placed on atoms 2,4,6,8 or 15 which are those atoms calculated to have a net positive charge. Structure (c) is the most important of the excited structures, since oxygen atom 16 has the greatest net negative charge.



(c) (d)

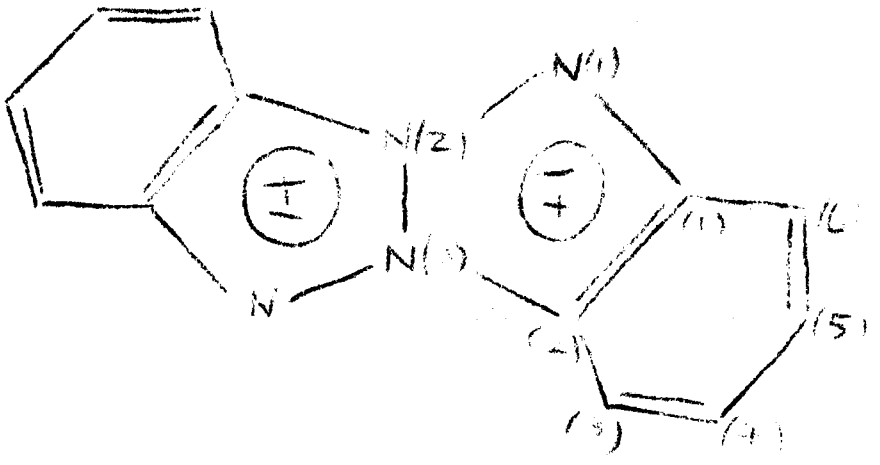
14.2 Vaciago's Molecules and derivatives.

Molecules with the empirical formulae $R_2R'_2C_4N_4$ were first described by Metze (1956) and by Pfleger et al. (1956,1957). They were first thought to be derivatives of tetraazacyclooctatetraene I



I

In 1962, however, Carboni and Castle (1962) synthesized a compound which they concluded from chemical evidence and n.m.r spectroscopy to be dibenzo-1,3a,4,6a - tetraazapentalene with structure II.



II

No Kekulé structure can be drawn for this system and it is best described chemically as a mesoionic system. II was found to be stable to heat and not to behave as a conjugated diene (Cf dibenzopentalene itself - Blood and Linstead (1952)).

Independently Vaciago in Rome had obtained samples from Pfleger of molecules with analyses:

$$\begin{matrix} R_1 \\ R_2 \end{matrix} \gtrless [C_4 N_4] \lessgtr \begin{matrix} R_2 \\ R_1 \end{matrix}$$

where: (a) $R_1 = CH_3$ $R_2 = COORb$

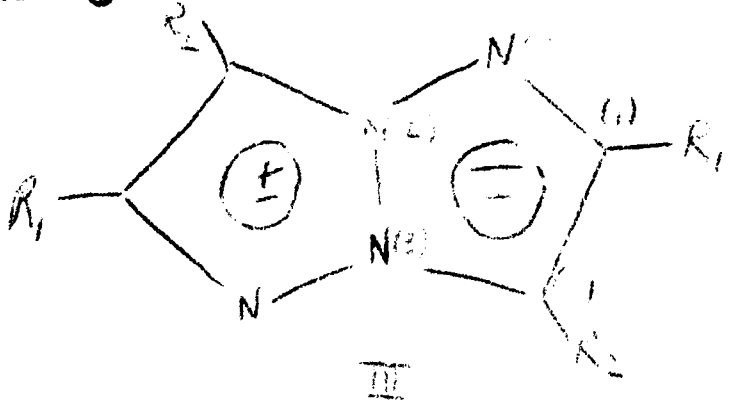
(b) $R_1 = CH_3$ $R_2 = Br$

(c) $R_1 = COORb$ $R_2 = H$

and with his collaborators has undertaken crystallographic analyses. Preliminary results have been reported (Brufani, Fedeli, Giacomello and Vaciago 1963 a,b,c,d) giving approximate bond lengths derived from 2-dimensional analysis.

These unrefined results show clearly that in all three molecules the structure is as III, which is

exactly analogous to II.



III

Refinement of the structure of (a) proved impossible because of excessive twinning. Molecule (b) which is non-centrosymmetric in the crystal and (c) which is centrosymmetric are capable of refinement and results for (c) with an estimated standard deviation of 0.01Å in the bond lengths have been obtained (Brufani et al 1964).*

The structure of II has been determined by Burke, Sparks and Trueblood (1963) and the bond lengths observed have been correlated by them with HMO bond orders which they have calculated.

Before it was known that Burke et al had done these calculations I used HMO Programme C for calculations on III and II using the following parameters for the heteroatoms and bonds.

$h_N' = 0.5$
$h_N'' = 1.5$
$k_{NN} = 1$
$k_{CN} = 0.8$

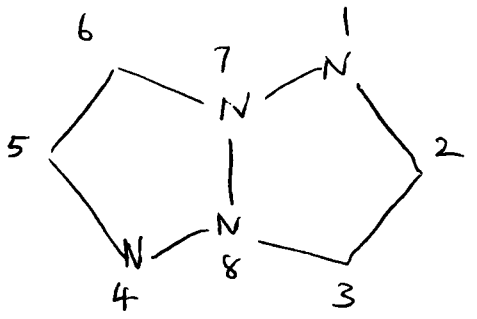
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* I should like to acknowledge a very useful conversation with Prof. Vaciago in May 1964 during which he explained very lucidly the state of the work on these molecules.

6a

ITALIAN MOLECULE

(tetra-aza-pentalene,



ENERGY

	S=o	
I	3.2892240	AU-So
2	I.8I53443	BG-Ao
3	I.3966024	BG-Ao
4	0.8747I8I	AU-So
5	0.2893763	AU-So
6	-0.8966025	BG-Ao
7	-I.3I53443	BG-Ao
8	-I.4533I85	AU-So

TOTAL PI ENERGY

I5.3305303

COEFFICIENTS

	I	2	3	4	5	6
E	3.28922	I.8I534	I.3966o	0.87472	0.28938	-0.89660
	AU-So	BG-Ao	BG-Ao	AU-So	AU-So	BG-Ao
I	0.25480	0.4II49	-0.32330	-0.2737I	0.5326I	-0.47406
2	0.I3006	0.03768	-0.47406	-0.5204I	-0.09564	0.32330
3	0.32397	-0.26080	-0.40343	-0.23624	-0.45377	0.08938
7	0.60663	0.5IIII	0.08938	0.3I376	-0.03567	0.40343

	7	8
E	-I.3I534	-I.45332
	BG-Ao	AU-So
I	-0.03768	0.27656
2	0.4II49	-0.45068
3	-0.5IIII	0.43373
7	-0.26080	-0.I7967

BOND ORDERS

I	2	0.58681
I	7	0.46223
2	3	0.75380
6	7	0.49457
7	8	0.39699

CHARGES

I	I.39473
2	I.04608
3	I.08530
7	I.47389

FREE VALENCES

I	0.6830I
2	0.39I44
3	0.48369
7	0.37827

POLARIZABILITIES

ATOM-ATOM

	1	2	3	7
1	-0.45678	0.12721	0.02544	0.03481
2	0.12721	-0.42266	0.22540	0.03449
3	0.02544	0.22540	-0.44105	0.02071
4	0.13387	0.00820	0.07318	0.05408
5	0.00820	0.02406	0.00067	0.00263
6	0.07318	0.00067	0.03427	0.06138
7	0.03481	0.03449	0.02071	-0.24305
8	0.05408	0.00263	0.06138	0.03493

BOND-BOND

		1 -2	1 -7	2 -3	6 -7	7 -8
1	-2	-0.33592	0.03583	0.23546	0.07057	0.01263
1	-7	0.03583	-0.30097	-0.01323	0.06854	0.01064
2	-3	0.23546	-0.01323	-0.21137	-0.04440	-0.03459
3	-8	-0.10317	-0.02546	0.15634	0.07355	0.03379
4	-5	0.06659	0.00262	-0.05283	-0.10317	0.01263
4	-8	0.00262	0.14029	-0.00560	-0.02546	0.01064
5	-6	-0.05283	-0.00560	0.03346	0.15634	-0.03459
6	-7	0.07057	0.06854	-0.04440	-0.28017	0.03379
7	-8	0.01263	0.01064	-0.03459	0.03379	-0.20812

ATOM-BOND

		1	2	3	7
1	-2	0.27972	0.07913	-0.18166	-0.08746
1	-7	0.31065	-0.13368	0.05976	0.17904
2	-3	-0.16694	0.00440	0.07000	0.05291
3	-8	0.10681	-0.07972	0.13706	-0.06257
4	-5	-0.08271	-0.03042	-0.01752	0.04091
4	-8	-0.17784	0.01901	-0.16036	-0.09658
5	-6	0.06904	0.01449	0.01200	-0.05589
6	-7	-0.17023	-0.01650	-0.05707	0.14224
7	-8	-0.10098	0.02965	-0.07450	0.14582

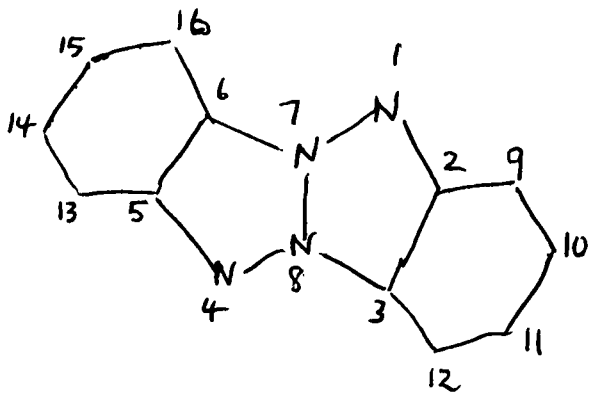
61c

DIBENZ-VACIACO

(dibenz-tetra-aza-; entalene)

ENERGY

	S-O	
1	2.[illegible]6077	AU-So
2	2.[illegible]91[illegible]	BG-Ao
3	1.[illegible]4706	AU-So
4	1.8560[illegible]9	BG-Ao
5	1.[illegible]9908[illegible]	BG-Ao
6	1.[illegible]49076	AU-So
7	0.8[illegible]5335	BG-Ao
8	0.8[illegible]3[illegible]16	AU-So
9	0.[illegible]586	AU-So
10	-0.[illegible]4200	BG-Ao
11	-1.[illegible]8[illegible]	AU-So
12	-1.[illegible]8[illegible]896	BG-Ao
13	-1.223751[illegible]	AU-So
14	-1.2807627	BG-Ao
15	-2.0891067	BG-Ao
16	-2.1278461	AU-So



TOTAL PI ENERGY

[illegible]6.8[illegible]6905

COEFFICIENTS

	1	2	3	4	5	6
E	3.[illegible]1061	2.[illegible]8[illegible]	1.86047	1.8560[illegible]	1.[illegible]9909	1.[illegible]15[illegible]91
	AU-So	BG-Ao	AU-So	BG-Ao	BG-Ao	AU-So
1	0.248[illegible]53	-0.[illegible]0[illegible]8[illegible]	-0.01[illegible]18	0.44[illegible]41	-0.18458	-0.[illegible]1[illegible]90[illegible]
2	0.14815	-0.28136	0.[illegible]4207	0.[illegible]29[illegible]66	-0.30367	-0.34582
3	0.[illegible]4509	-0.[illegible]67[illegible]0	0.[illegible]50[illegible]7	-0.[illegible]3364	-0.[illegible]6420	0.09634
7	0.[illegible]8722	0.[illegible]3[illegible]73	-0.[illegible]1295	0.41891	0.[illegible]1[illegible]9[illegible]	0.[illegible]1[illegible]54
9	0.05201	-0.23364	0.[illegible]1[illegible]3	0.[illegible]9428	0.04774	-0.20648
10	0.02528	-0.[illegible]1828	0.[illegible]3716	0.[illegible]1110	0.[illegible]6092	0.[illegible]0[illegible]41
11	0.[illegible]2[illegible]44	-0.[illegible]3346	0.31594	0.04896	0.38503	0.[illegible]0042
12	0.[illegible]6[illegible]08	-0.[illegible]8096	0.[illegible]5064	-0.[illegible]0402[illegible]	0.10076	0.[illegible]4[illegible]55

	7	8	9	10	11	12
E	0.8[illegible]853	0.[illegible]1383	0.22446	-0.55442	-1.04268	-1.[illegible]8819
	BG-Ao	AU-So	AU-So	BG-Ao	AU-So	BG-Ao
1	0.[illegible]9603	0.[illegible]0767	0.[illegible]5655	0.37553	0.06076	0.16[illegible]84
2	-0.[illegible]1[illegible]56	-0.26170	0.[illegible]0192	-0.[illegible]5669	-0.18544	-0.37621
3	0.13767	-0.36475	-0.20410	0.[illegible]0583	-0.25426	0.[illegible]2119
7	0.16273	0.[illegible]1177	-0.[illegible]5489	-0.[illegible]5062	0.[illegible]5462	0.[illegible]3[illegible]84
9	-0.39370	0.[illegible]4563	-0.24071	-0.[illegible]7483	0.39901	0.[illegible]7[illegible]98
10	-0.22244	0.[illegible]8022	-0.[illegible]5595	0.20[illegible]06	-0.[illegible]3059	0.29388
11	0.[illegible]0273	0.16380	0.22815	0.[illegible]5892	-0.[illegible]1[illegible]57	-0.40[illegible]3
12	0.39[illegible]49	-0.24691	0.[illegible]0716	-0.[illegible]0717	0.[illegible]9593	0.16251

	13	14	15	16
E	-1.[illegible]3[illegible]75	-1.28076	-2.08920	-2.1278[illegible]
	AU-So	BG-Ao	BG-Ao	AU-So
1	-0.20744	-0.[illegible]4417	0.[illegible]5337	0.[illegible]953
2	0.[illegible]3943[illegible]	0.[illegible]5023	-0.[illegible]3[illegible]55	-0.33206
3	-0.[illegible]4738	0.31610	0.33469	0.[illegible]3794
7	0.[illegible]2[illegible]11	0.[illegible]1462	0.[illegible]0865	-0.[illegible]0[illegible]1
9	0.[illegible]5305	-0.[illegible]1[illegible]18	0.[illegible]6723	0.[illegible]6701
10	-0.35925	0.[illegible]5087	-0.[illegible]4975	-0.[illegible]2610
11	0.[illegible]8658	-0.[illegible]0[illegible]8[illegible]	0.[illegible]4541	0.[illegible]3527
12	-0.[illegible]1[illegible]83	-0.[illegible]4046	-0.[illegible]8[illegible]04	-0.[illegible]6473

BOND ORDERS

1	2	0.[illegible]0871
1	7	0.[illegible]6592
2	3	0.[illegible]4771
2	9	0.[illegible]7684
3	10	0.[illegible]9106
6	7	0.[illegible]2782
7	8	0.[illegible]1382
9	10	0.[illegible]1085
10	11	0.[illegible]1821
11	12	0.[illegible]0379

CHARGES

1	1.[illegible]0760
2	1.[illegible]1240
3	1.[illegible]1152
7	1.[illegible]2278
9	1.[illegible]2267
10	1.[illegible]1229
11	1.[illegible]2251
12	1.01623

FREE VALENCES

1	0.[illegible]5743
2	0.[illegible]0880
3	0.[illegible]5546
7	0.[illegible]1[illegible]0
9	0.[illegible]1[illegible]6
10	0.[illegible]0[illegible]0
11	0.[illegible]0995
12	0.43719

The complete results are given in the accompanying tables. The bond orders and lengths derived from them using the formulae: $l = 1.567-0.267p$ (Cruickshank and Sparks (1960)) and $r_N = r_C-0.045Å$ (Burke et al 1963) are extracted in table 14.2 where the atoms are given the 'crystallographic' numbering of Brufani et al (1963 a). II is numbered to correspond with this and so its numbering differs from that of Burke et al. Also given are the crystallographic bond lengths from Brufani et al (1964) and Burke et al (1963).

Table 14.2 - Bond orders and lengths.

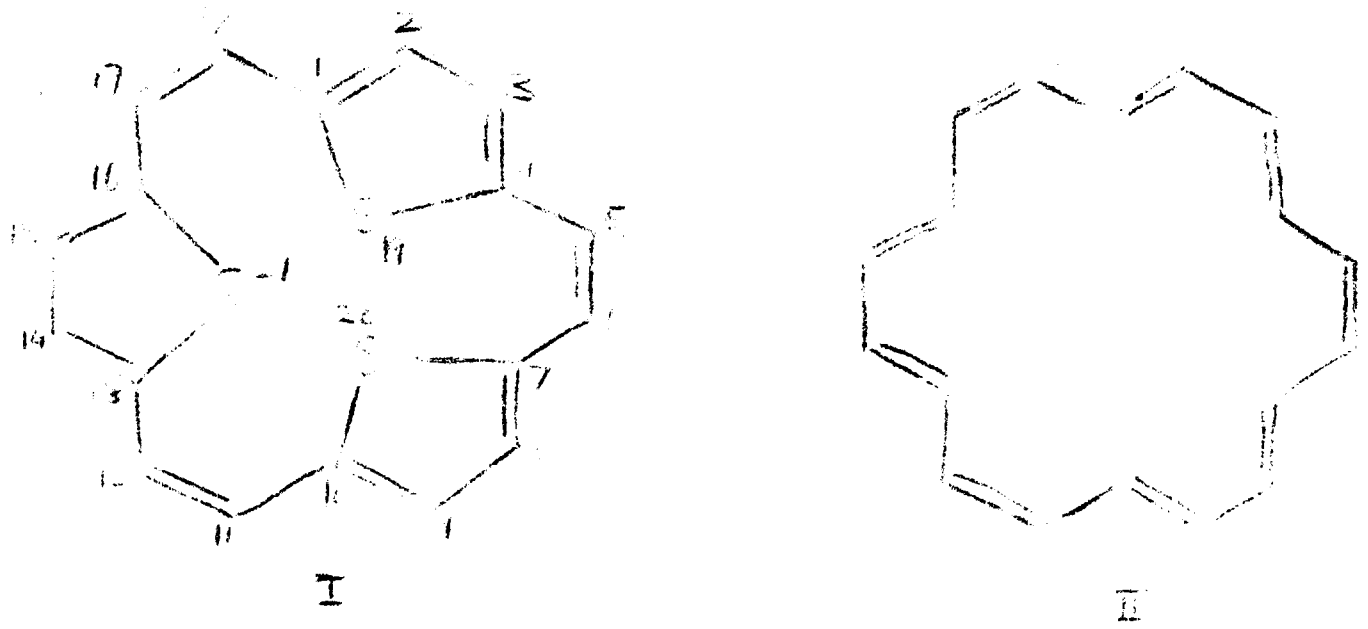
	Molecule III			Molecule II		
Bond	Bond Order	Bond length Calc.	Obs.	Bond Order	Bond length Calc.	Obs.
N(1)-N(2)	.462	1.354	1.33	.466	1.353	1.34
N(2)-N(3)	.397	1.371	1.35	.414	1.366	1.35
N(1)-C(1)	.587	1.365	1.35	.509	1.386	1.38
N(3)-C(2)	.495	1.390	1.38	.438	1.405	1.39
C(1)-C(2)	.754	1.366	1.37	.548	1.421	1.41
C(1)-C(6)		———		.577	1.413	1.39
C(2)-C(3)		———		.591	1.409	1.40
C(3)-C(4)		———		.704	1.379	1.38
C(4)-C(5)		———		.618	1.402	1.42
C(5)-C(6)		———		.711	1.377	1.38

The degree of agreement for molecule II is not significantly different from that obtained by Burke et al using slightly different parameters.

The approximate equality of the two N-N bond orders in molecule II is in excellent agreement with the observed absence of diene behaviour.(The corresponding

bonds in dibenzpentalene have orders 0.467,0.706).

14.3 [16] - Annulene trisulphide.



I II

Fig. 14.3

The molecule I (Fig 14.3) has been synthesized by Badger, Elix and Lewis (1964). HMO calculations have been done with three sets of values for the parameters h_S and k_{CS} using programme S (because of the threefold symmetry). The energy levels and charges, bond orders and free valences obtained are shown in the accompanying table. The molecular orbital coefficients were also calculated but are not given here.

Streitwieser (1961, Chap.5) does not recommend particular values for h_S and k_{CS} and so the following pairs of values, consistent with his ideas, were used:

(1) $h_S = 1.5 \quad k_{CS} = 1$

(2) $h_S = 2.0 \quad k_{CS} = 1$

(3) $h_S = 1.5 \quad k_{CS} = 0.8$

The system has 24 π-electrons which occupy in pairs the 12 bonding orbitals, which arise for all

63a

18-ANNULENE TRISULPHIDE
H=1.5, K=1

ENERGY

	S=0
1	2.7175678
2	2.6700617
3	2.6700616
4	1.6360102
5	1.6360101
6	1.2308802
7	1.1530851
8	1.1530848
9	1.0000004
10	1.0000002
11	0.2628020
12	0.2628018
13	-0.5604410
14	-0.5604411
15	-0.0000007
16	-1.4781474
17	-1.6805021
18	-1.6805026
19	-1.9739164
20	-1.9739164
21	-1.9999999

TOTAL PI ENERGY
34.8483444

BOND ORDERS			CHARGES		FREE VALENCES	
1	2	0.61908	1	1.01535	1	0.16498
1	18	0.51352	2	1.09366	2	0.44542
1	19	0.43153	5	1.04727	5	0.47785
2	3	0.66756	19	1.68742	19	0.86300
5	6	0.74067				

18-ANNULENE TRISULPHIDE
H=1.5
K=0.8

ENERGY

	S=0
1	2.5265281
2	2.4486958
3	2.4486958
4	1.6230763
5	1.6230761
6	1.2808434
7	1.1271380
8	1.1271378
9	1.0000005
10	1.0000003
11	0.2831961
12	0.2831964
13	-0.5013359
14	-0.5013360
15	-0.9999998
16	-1.3173710
17	-1.6339586
18	-1.6339586
19	-1.9267600
20	-1.9267601
21	-1.9999998

TOTAL PI ENERGY
33.8831703

BOND ORDERS			CHARGES		FREE VALENCES	
1	2	0.63003	1	1.00855	1	0.13687
1	18	0.54763	2	1.06699	2	0.44450
1	19	0.36752	5	1.03657	5	0.46992
2	3	0.65751	19	1.77576	19	0.99702
5	6	0.71450				

18-ANNULENE TRISULPHIDE

H=2
K=1

ENERGY

S=0

1	3.0000003
2	2.9477246
3	2.9477244
4	1.6574341
5	1.6574339
6	1.4142138
7	1.2689926
8	1.2689923
9	1.0000004
10	1.0000003
11	0.2786577
12	0.2786576
13	-0.5337643
14	-0.5337643
15	-0.9999997
16	-1.4142134
17	-1.6642517
18	-1.6642517
19	-1.9547003
20	-1.9547004
21	-1.9999998

TOTAL PI ENERGY

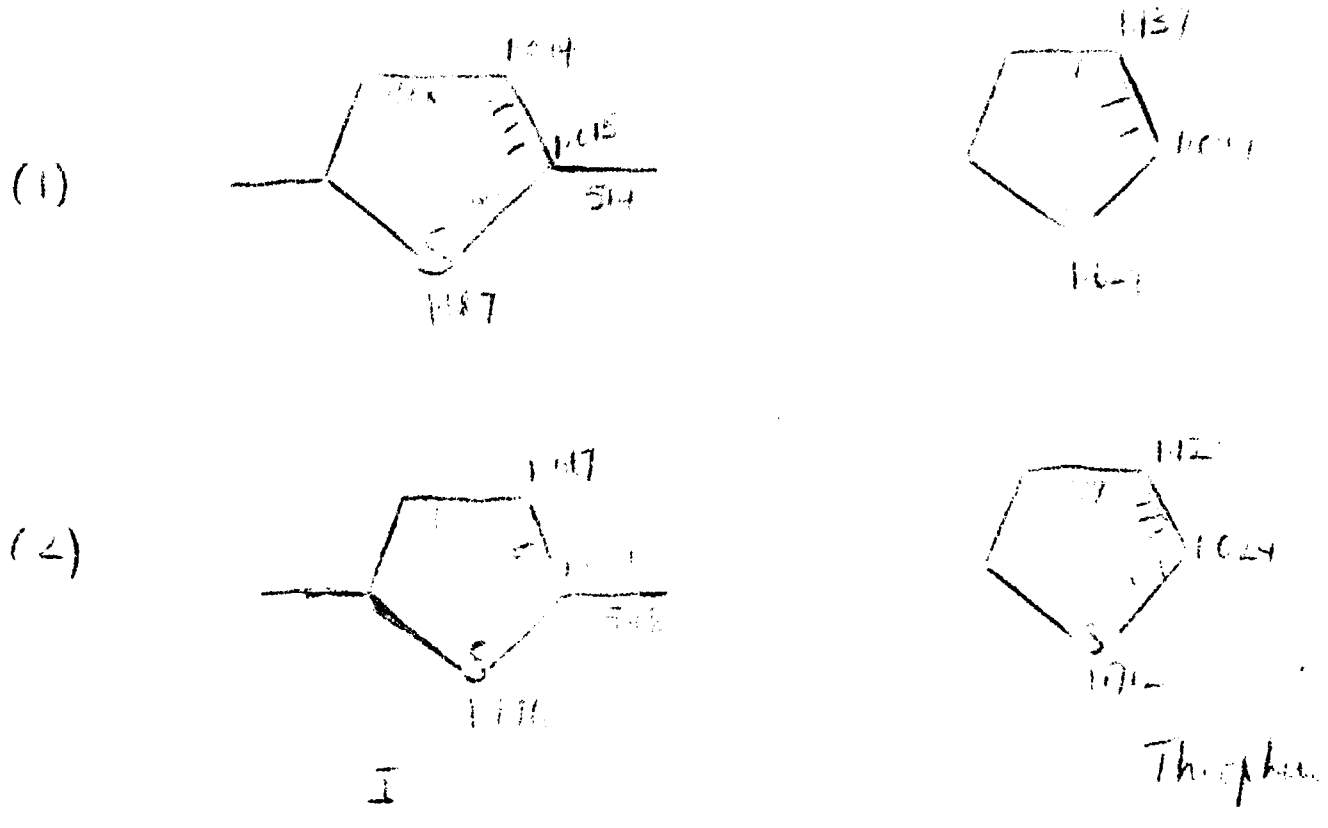
37.4396643

BOND ORDERS			CHARGES		FREE VALENCES	
1	2	0.63822	1	0.99848	1	0.18744
1	18	0.53227	2	1.07762	2	0.44177
1	19	0.38412	5	1.04231	5	0.47426
2	3	0.66206	19	1.76314	19	0.95383
5	6	0.72546				

three sets of parameters.

Charges and Bond Orders: The most striking point about these is the high bond order of the 5–6 bond. It is shown in Chapter II how refinements to the Hückel theory to introduce more self-consistency tend to reduce charge migration as predicted by the HMO method but enhance differences in bond order. Thus we may reasonably consider the 5–6 bond to approach an ethylenic bond in strength. This leads to effective isolation of the three thiophen units. The bonds 4–5, 1–18 etc. being relatively weak facilitate the twisting of the thiophen units out of the plane which may well be necessitated by steric interactions between the sulphur atoms. (Coulson and Haigh 1963).

Calculations using sets of parameters (1) and (2) for thiophen itself have also been carried out (see section 15) and the charges and bond orders obtained are shown in Fig.14.3a together with those obtained for the corresponding part of I.



Whereas the charge migrations have the same relative sizes, the need to form extra bonds changes the distribution of bond order so that the 2–3 bond of I (corresponding to the 3–4 bond in the usual chemical numbering of thiophen) becomes the strongest.

15. Study of the effect of varying the parameters in simple heterosystems.

Many different values for the atom and bond parameters h_r and k_{rs} have been used by various authors for calculations on heteromolecules of various sorts. However no systematic study of how the calculated energies, charges, bond orders etc. depend on these choices has been reported. Accordingly it was thought worth while, having the HMO programmes available, to carry out comparative studies on two of the simplest heterosystems, namely the pyrrole-like systems and the pyridine-like systems.

These systems both have a single heteroatom and calculations have been done taking the value of h for this atom between -2 and +2 and k for the bonds joining this atom to its neighbours in the range 0-2. Complete calculations were carried out for each pair of parameters: i.e. energies, M.o coefficients, charges, bond orders and the 3 polarizabilities. Some of the results for quantities most likely to be of interest are shown graphically in the accompanying diagrams.

No attempt has been made to make any correlations with experimental data for molecules in these classes as, to be done properly, this would have involved a full-scale review of an enormous amount of published work. References to a great deal of the work done on the choice of 'h' and 'k' for various particular molecules may be found in Chapter 5 of Streitwieser's book (1961).

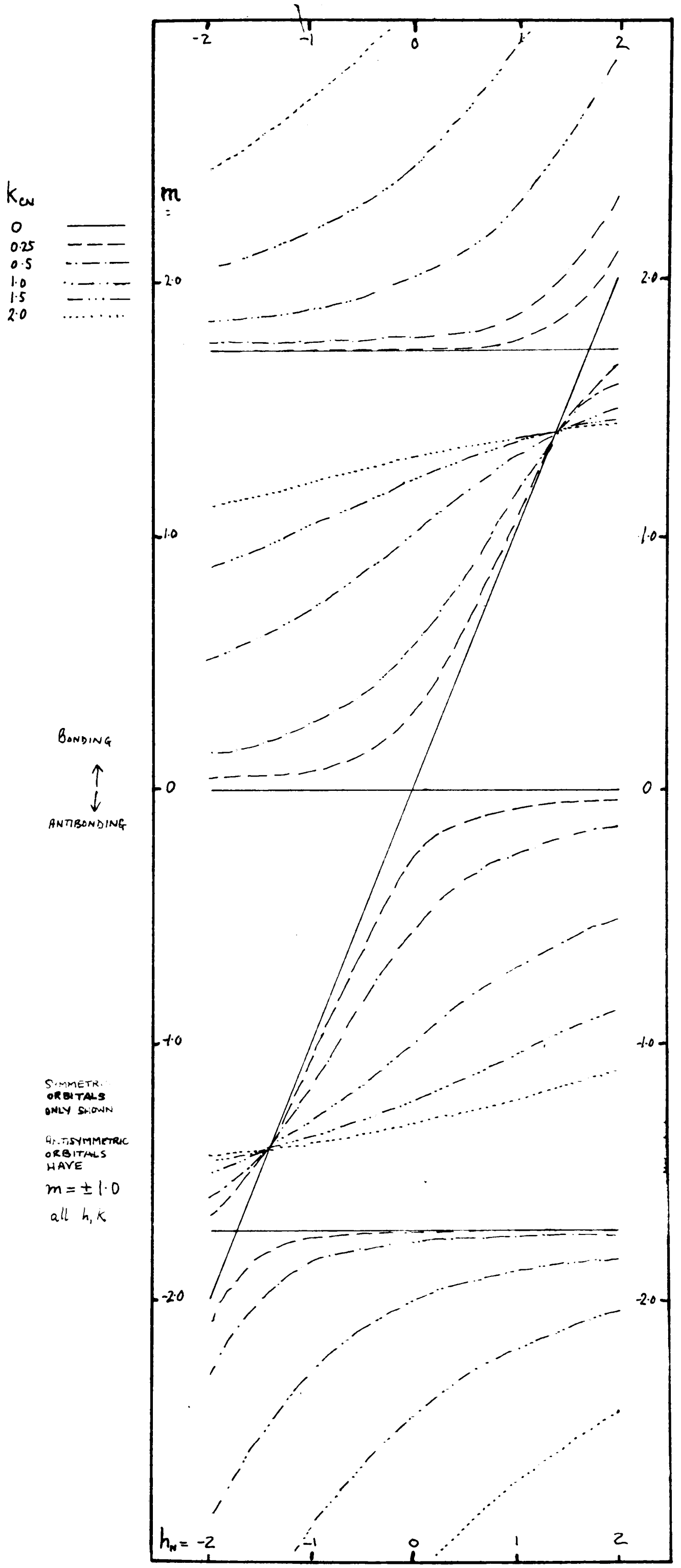


Fig 15·1a PYRIDINE ORBITALS

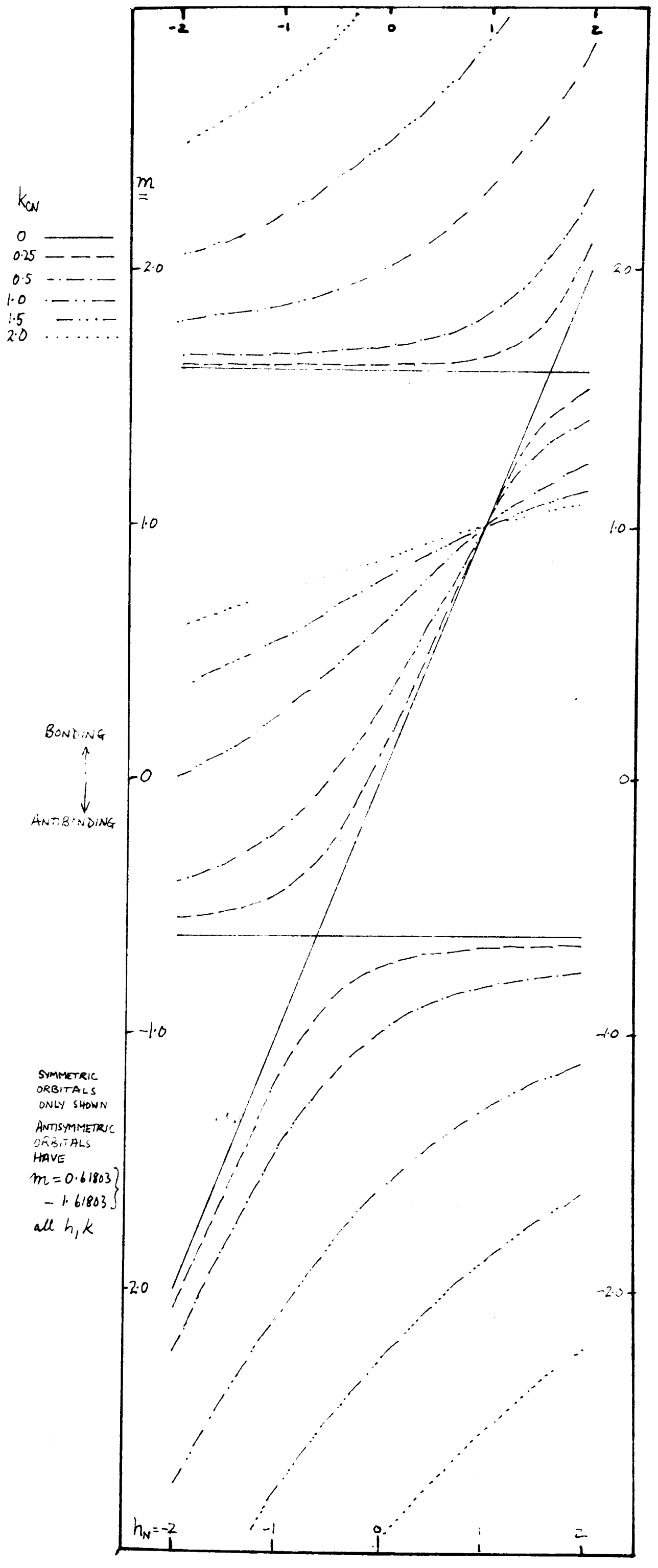
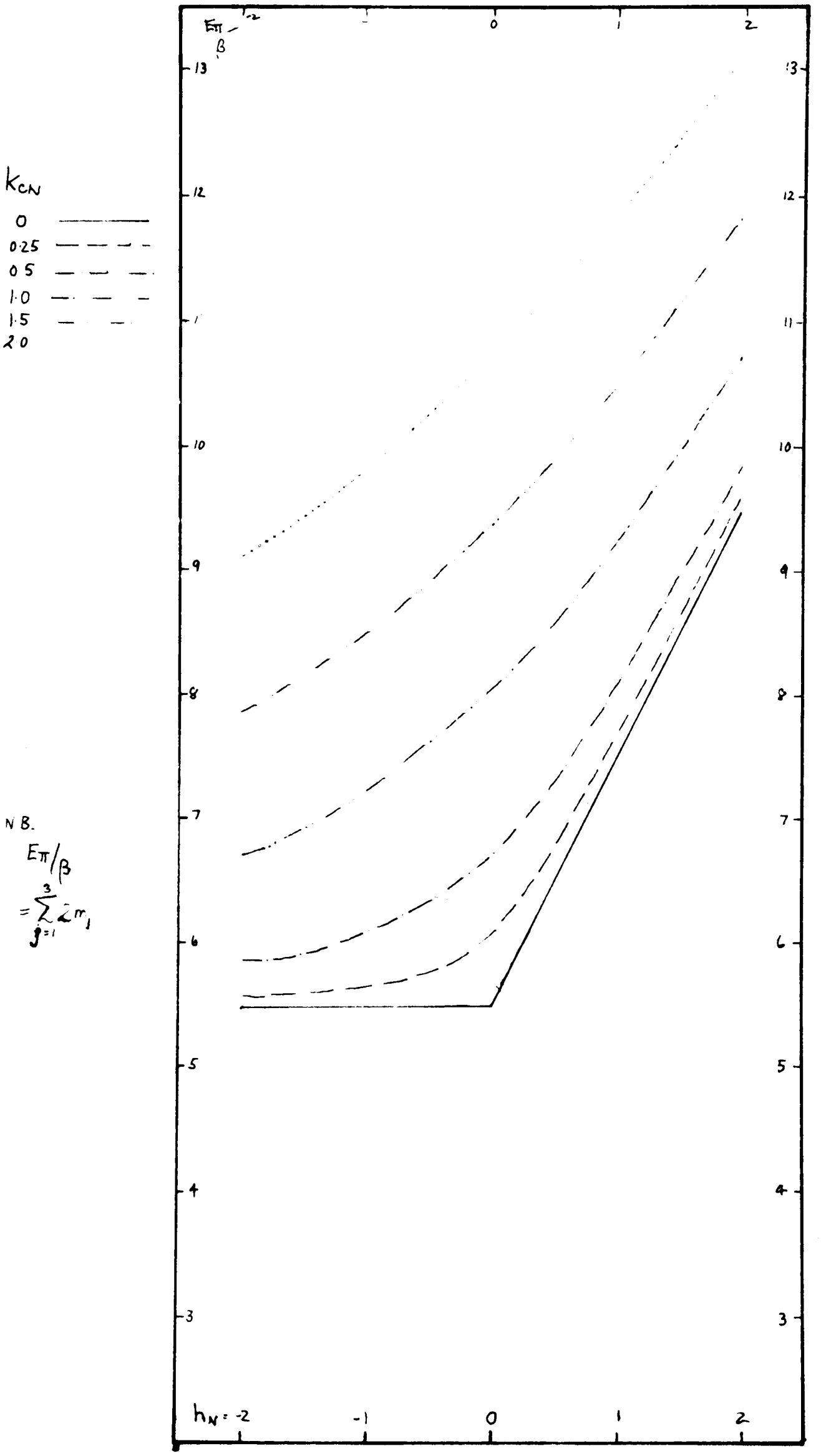


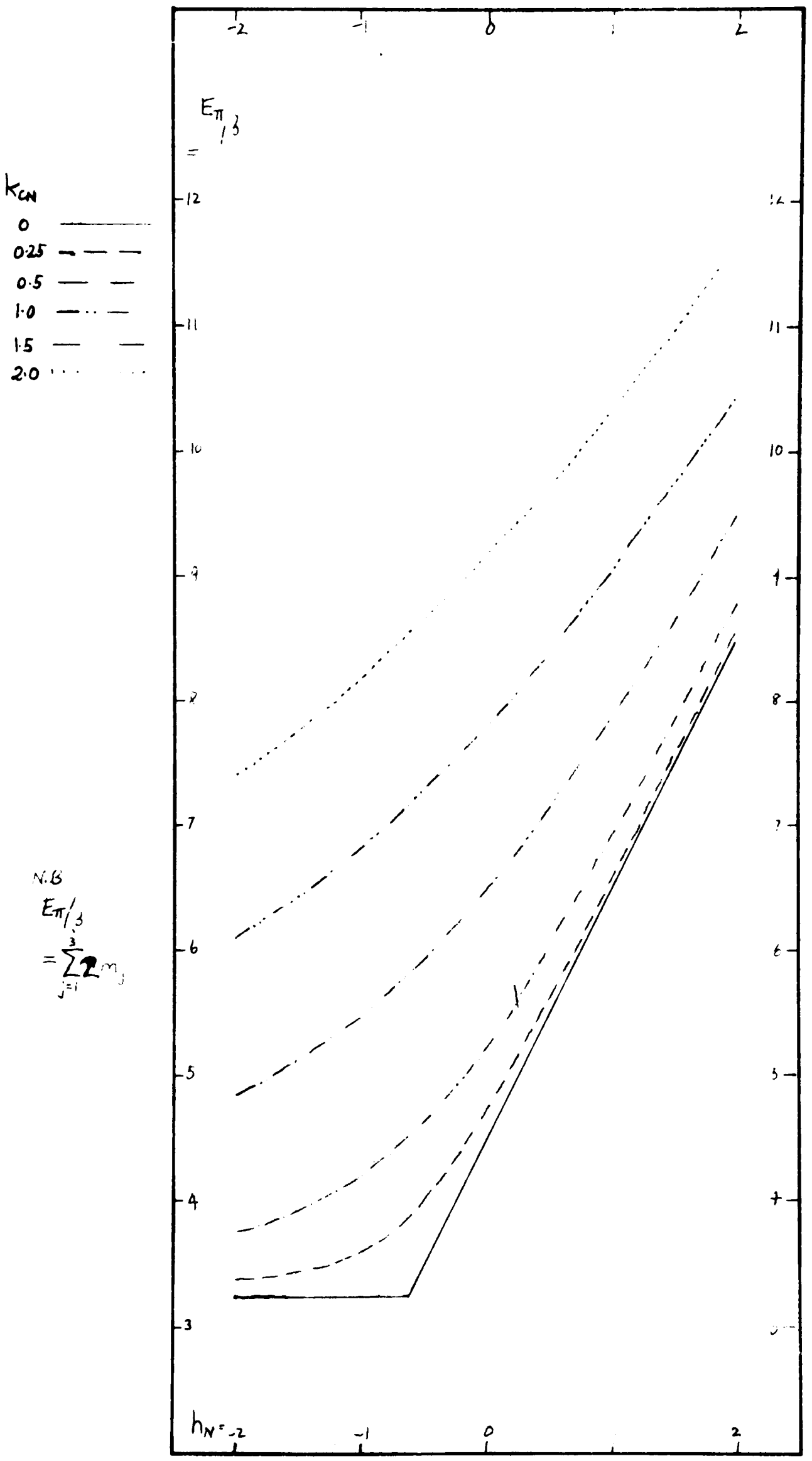
Fig 15·16 PYRROLE ORBITALS



N.B.

$E_\pi/\beta = \sum_{j=1}^{3} \alpha m_j$

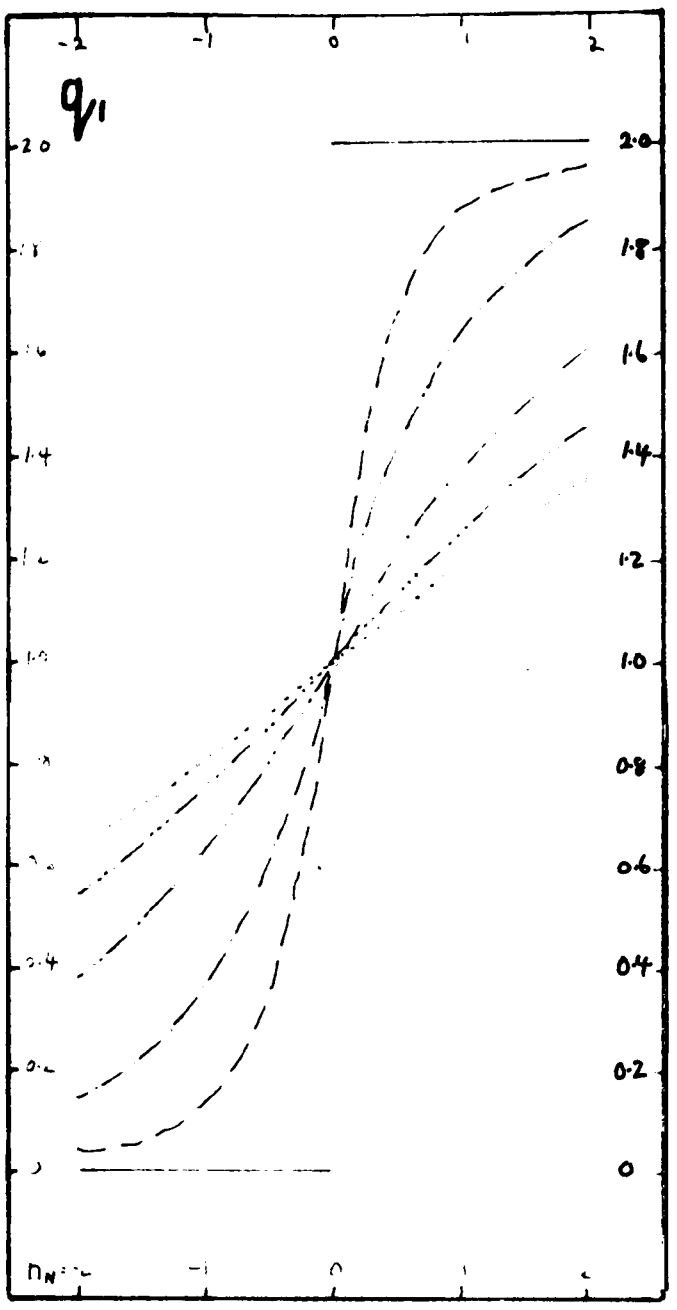
Fig 15·1c PYRIDINE - TOTAL π-ENERGY

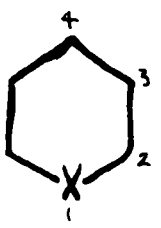


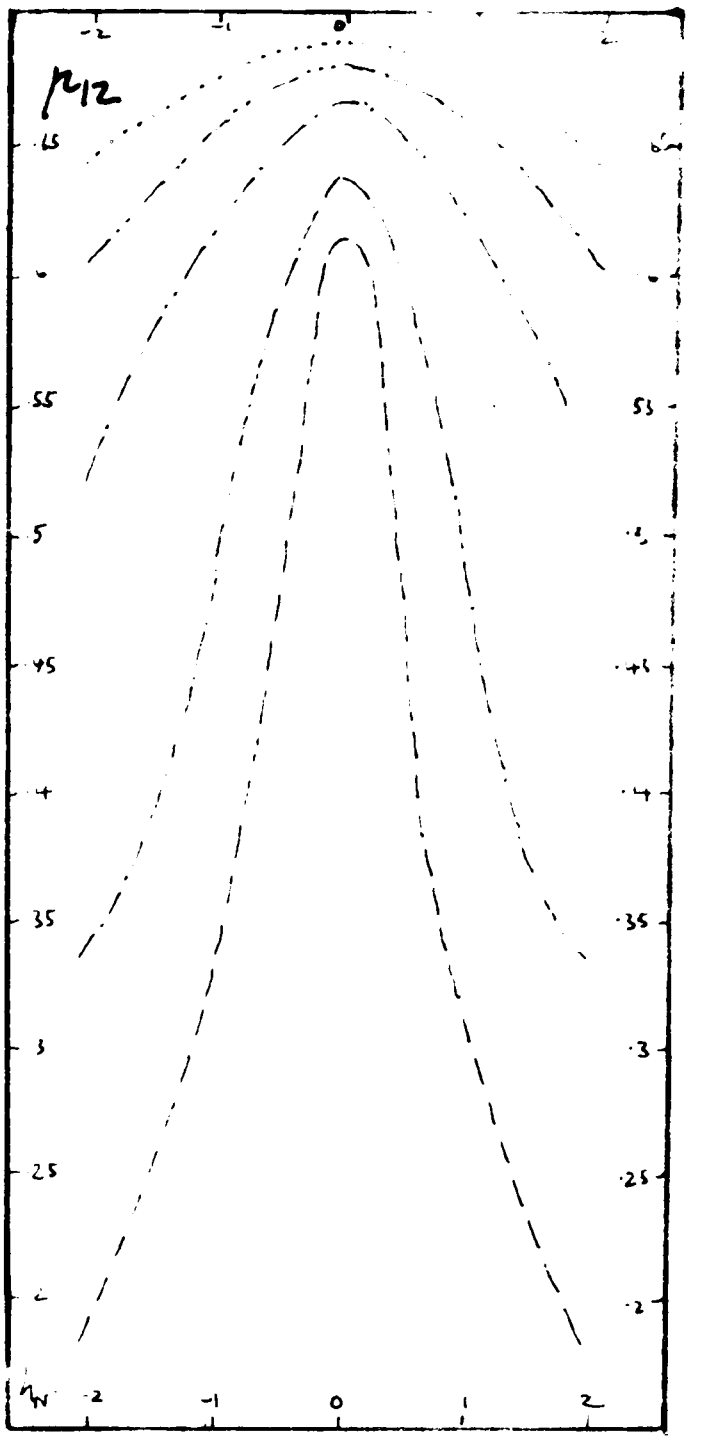
N.B

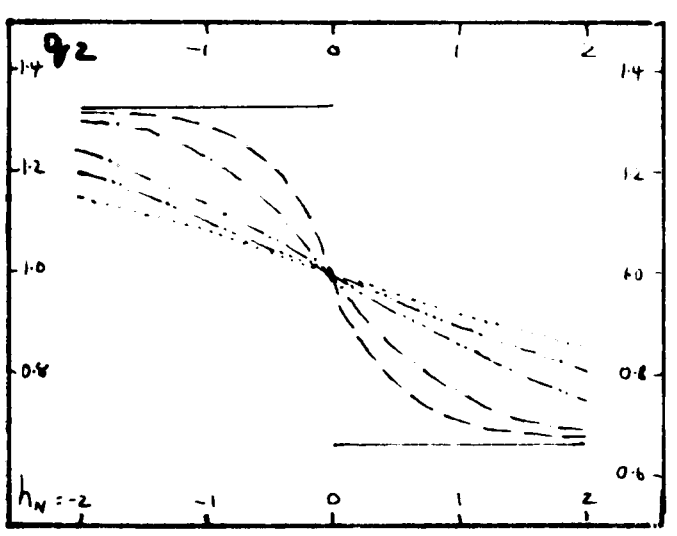
$E_{\pi/\beta} = \sum_{j=1}^{3} \varepsilon_j m_j$

Fig 15·1d PYRROLE - TOTAL π-ENERGY









K_{CN}

0

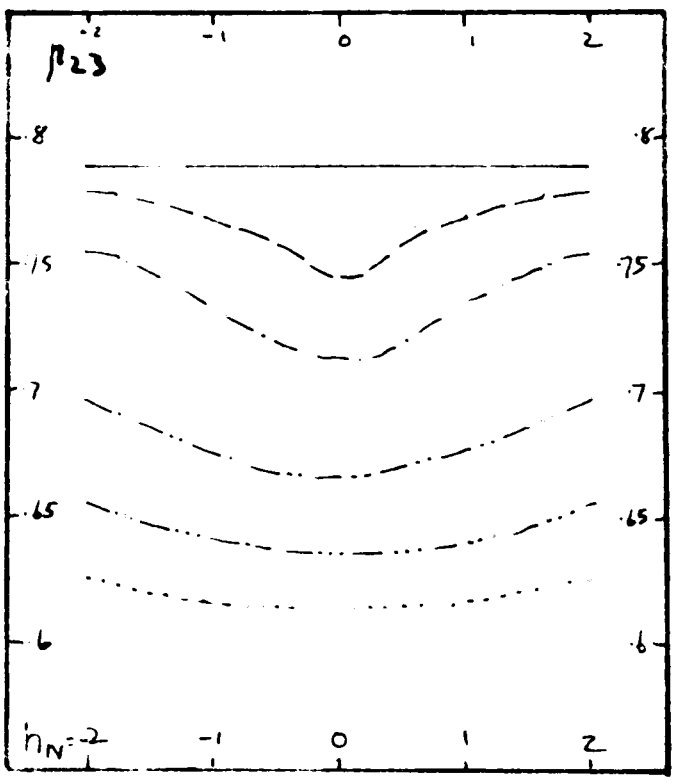
0.25

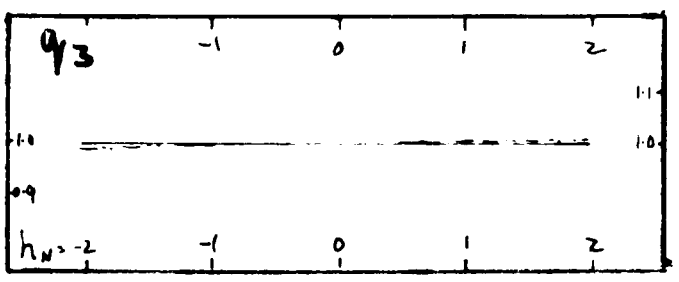
0.5

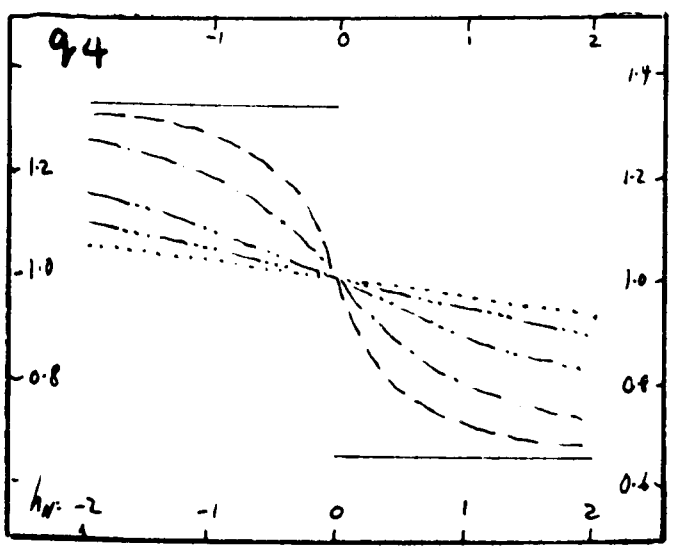
1.0

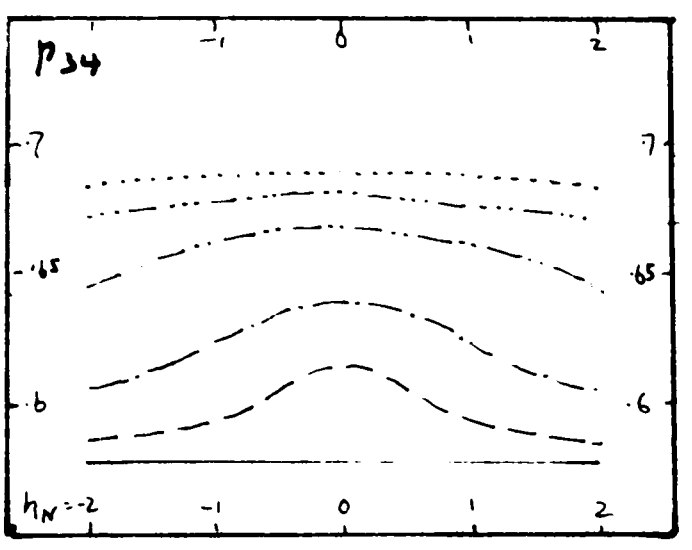
1.5

2.0







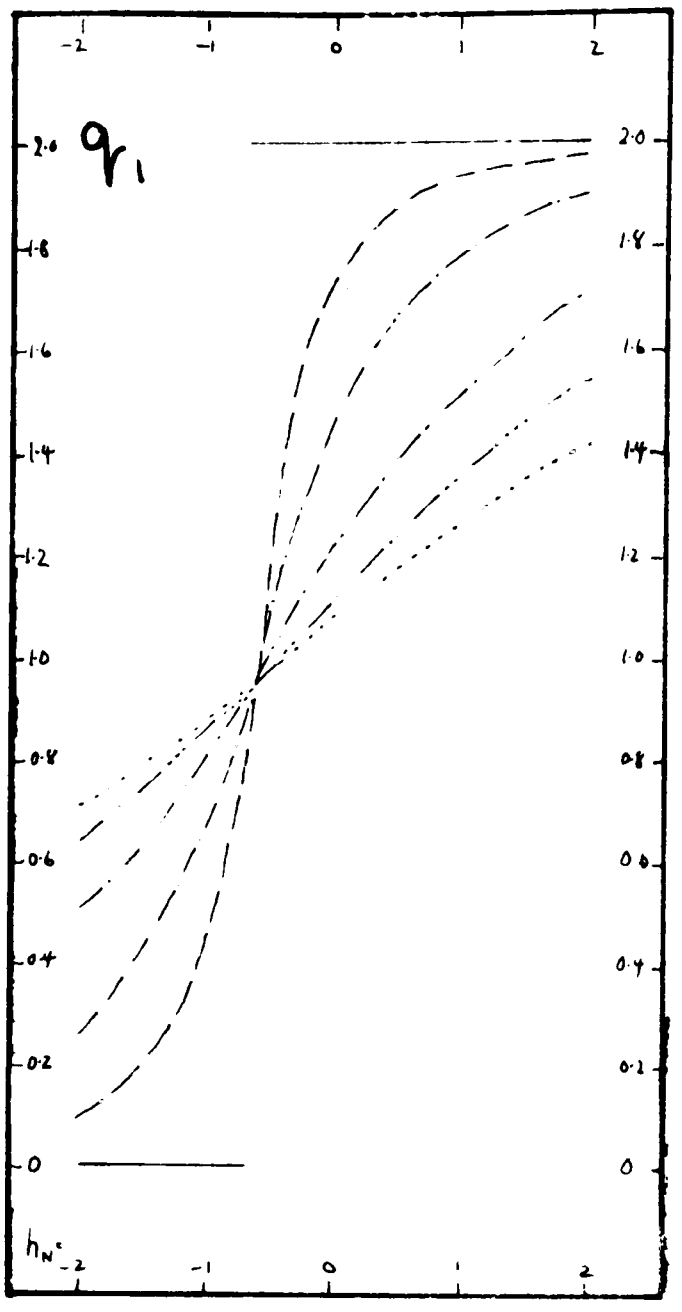


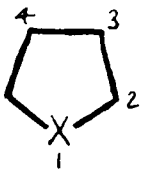
PYRIDINE - CHARGES

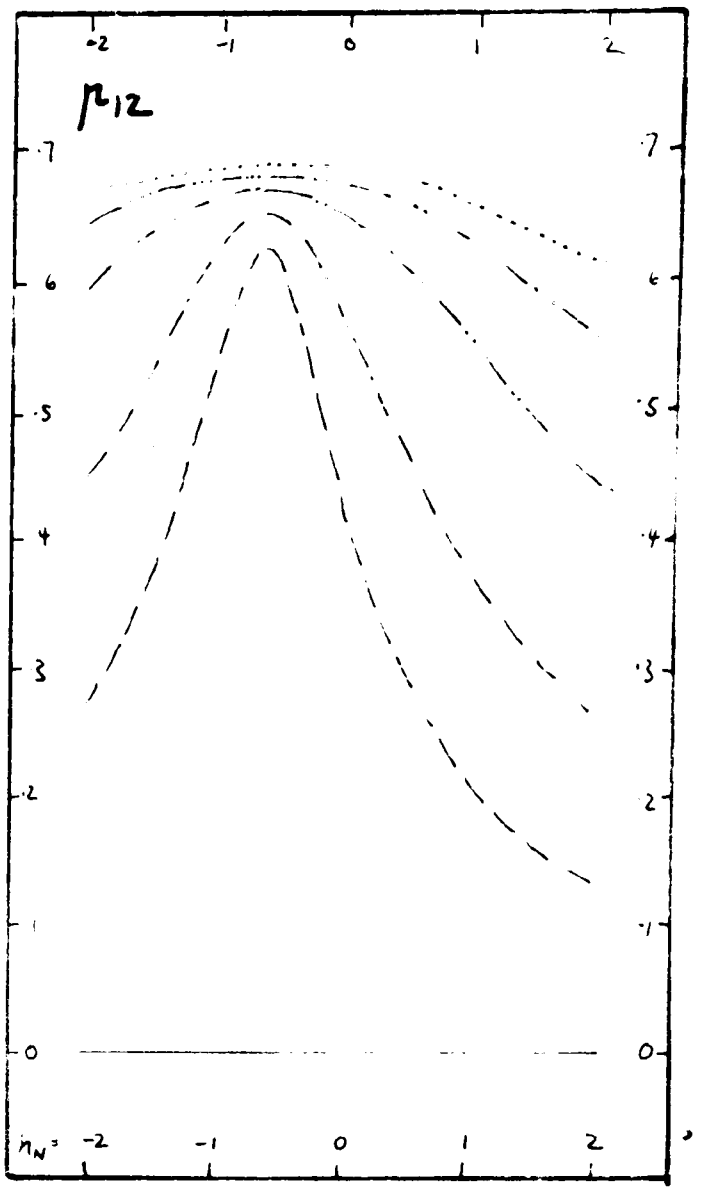
Fig 15.1e

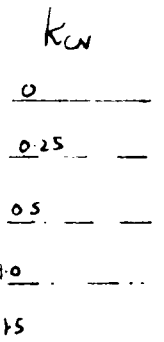
BOND ORDERS

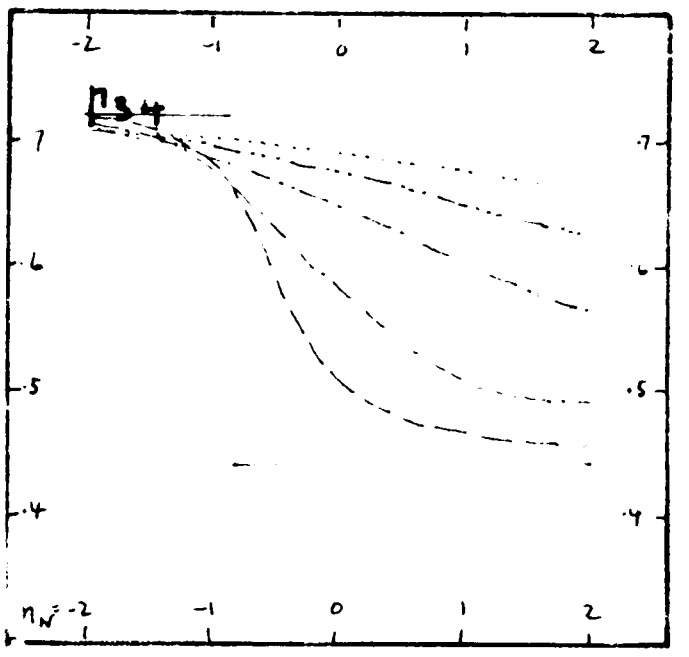
Fig 15.1f

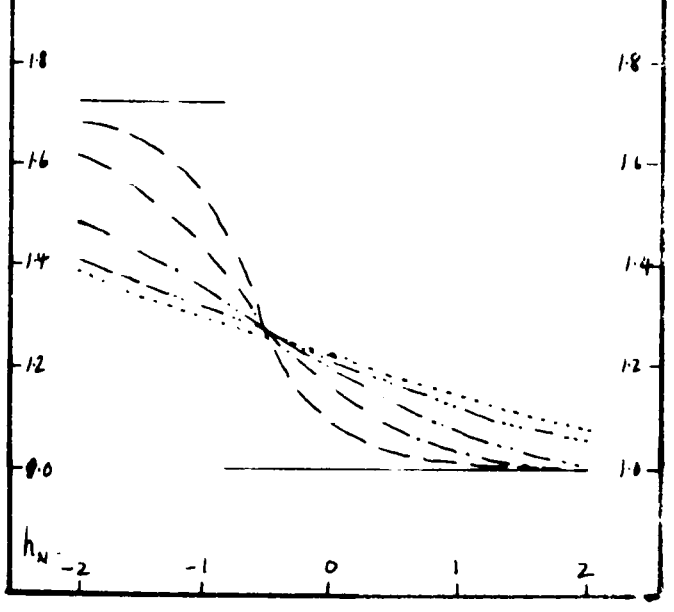


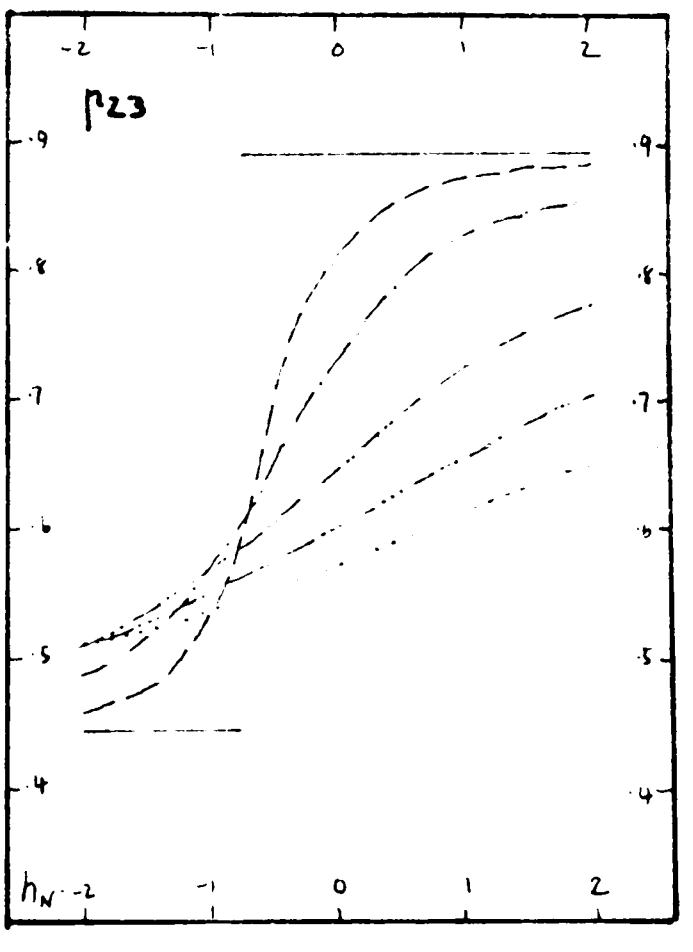


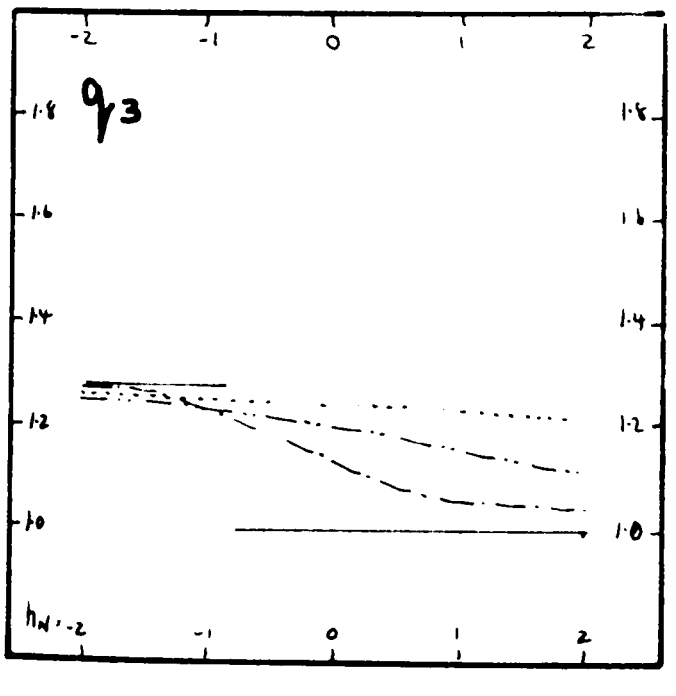












PYRROLE - CHARGES

Fig 15·1g

BOND ORDERS

Fig 15·1h

We do, however, discuss in 15.2 one method of attempting a choice of 'h' and 'k' which is unlikely to succeed.

As well as some of the results we shall give in 15.1 some generalizations concerning the numerical quantities for alternant heterosystems which made themselves apparent in the complete calculations done. *

15.1 Alternant heterosystems - some generalizations concerning positive and negative h.

The most conspicuous feature of the graphs of Huckel derived quantities for the pyridine-like molecules are the symmetries about the line h=0 for all k. These symmetries are summarized below:

1. Bonding Orbitals for h =+a are complementary to Antibonding orbitals for h =-a
2. The following quantities are unchanged when h changes sign:
   - p_{rs} r,s in different sets, not necessarily bonded
   - F_r all atoms r
   - $\pi_{r,s}$ all pairs of atoms r,s
   - $\pi_{rs,tu}$ all pairs of bonds rs,tu
3. The following quantities change sign:
   - q_r-1 all atoms r

- - - - - - - - - - - - - -

* Some of the results of this section are implicit in the work of Greenwood (1952) who used the complex integral formulation of Coulson and Longuet-Higgins (1947a) in the proofs.

p_{rs} r,s in same set

$\pi_{r,st}$ all atom-bond pairs

The conditions under which 2 and 3 follow from 1 and the types of molecule for which 1 holds may be derived as follows:

Assume that p_{rs} is an even function of h for all k. It follows immediately from (2.3) that F_r has this property and from (2.4) that $\pi_{rs,tu}$ has it. Similarly if we assume that $q_r - 1$ is an odd function it follows from (2.4) that $\pi_{r,st}$ is odd and since dh is odd that $\pi_{r,s}$ is even. Let us now assume only that 1 is true. Then for any r,s in the same set

$$c_{rj}c_{sj}(h) = c_{r,n+1-j}c_{s,n+1-j}(-h) \quad \text{for all } j \qquad (15.1)$$

and for any r,s in different sets

$$c_{rj}c_{sj}(h) = -c_{r,n+1-j}c_{s,n+1-j}(-h) \quad \text{for all } j \qquad (15.2)$$

Now any matrix of eigenvector coefficients $\underset{\sim}{C}$ is unitary.

Hence $\sum_{j=1}^{n} c_{rj}c_{sj} = \delta_{rs}$

$$q_r(-h) - 1 = \sum_{j=1}^{m} 2\, c^2_{rj}(-h) - 1 \quad , \text{ } 2m\ \pi\text{-electrons in molecule}$$

$$= 2 - \sum_{j=m+1}^{n} 2c^2_{rj}(-h) - 1$$

$$= 1 - \sum_{j=1}^{m} 2c^2_{rj}(h) \quad , 2m=n$$

$$= -(q_r(h) - 1) \qquad (15.3)$$

$$p_{rs}(-h) = \sum_{j=1}^{m} 2c_{rj}c_{sj}(-h)$$

$$= -\sum_{j=m+1}^{n} 2c_{rj}c_{sj}(-h)$$

$$= \mp \sum_{j=1}^{m} 2c_{rj}c_{sj}(h) \quad , 2m=n$$

Upper sign if r,s in different sets.

$$= \pm\ p_{rs}(h) \qquad (15.4)$$

Both these results may be extended to the case where n is odd provided that the molecule still has exactly n π-electrons. They thus do <u>not</u> apply to the majority of odd systems which have an even number of π-electrons. We have thus shown that for any alternant heteromolecule with a number of π-electrons equal to that of π-centres the properties 2 and 3 follow from property 1. We shall now show the conditions for property 1.

If the atoms of one set are numbered 1 to g and those of the other from g+1 to n, the secular matrix $\underset{\sim}{H}$ may be partitioned thus:

$$\underset{\sim}{H} = \begin{bmatrix} \underset{\sim}{D}^{\circ} & \underset{\sim}{B} \\ \underset{\sim}{B}^{\dagger} & \underset{\sim}{D}^{*} \end{bmatrix} \qquad (15.5)$$

Where $\underset{\sim}{D}^{\circ}$ and $\underset{\sim}{D}^{*}$ are diagonal matrices with elements h_r; and $\underset{\sim}{B}$ and its transpose $\underset{\sim}{B}^{\dagger}$ contain all the non-zero k_{rs}. The eigenvectors of $\underset{\sim}{H}$ may likewise be partitioned:

$$\underline{c} = \begin{bmatrix} \underline{u} \\ \underline{v} \end{bmatrix} \qquad (15.6)$$

The eigenvalues λ satisfy the equations

$$\begin{aligned} +\underset{\sim}{D}^{\circ}\ \underline{u} + \underset{\sim}{B}\underline{v} &= \lambda\,\underline{u} \\ \underset{\sim}{B}^{\dagger}\ \underline{u} + \underset{\sim}{D}^{*}\ \underline{v} &= \lambda\,\underline{v} \end{aligned} \qquad (15.7)$$

The complementary orbital to $\underline{c}$ is $\begin{pmatrix} \underline{u} \\ -\underline{v} \end{pmatrix}$ with eigenvalue $-\lambda$

this satisfies the equations;

$$\begin{aligned} -\underset{\sim}{D}^{\circ}\ \underline{u} + \underset{\sim}{B}\,(-\underline{v}) &= -\lambda\,\underline{u} \\ \underset{\sim}{B}^{\dagger}\ \underline{u} + (-\underset{\sim}{D}^{*})(-\underline{v}) &= -\lambda\,(-\underline{v}) \end{aligned} \qquad (15.8)$$

or

$$\begin{bmatrix} -\mathfrak{D}^{\circ} & \mathfrak{B} \\ \mathfrak{B}^{\dagger} & -\mathfrak{D}^{*} \end{bmatrix} \begin{bmatrix} \underline{u} \\ -\underline{v} \end{bmatrix} = \rightarrow \begin{bmatrix} \underline{u} \\ -\underline{v} \end{bmatrix} \qquad (15.8a)$$

These are the secular equations for the same system as $\mathfrak{H}$ but with all the diagonal terms h_r changed in sign. The condition for property 1 to hold is thus that all atom parameters h_r must change sign, leaving all bond parameters k_{rs} unchanged.

15.2 The impossibility of choosing values of 'h' and 'k' from charges and bond orders alone.

A study of the results reveals that any particular charge distribution and set of bond orders which may be predicted for a certain pair of values h_o, k_o of h,k may also be predicted approximately for any other value of h, if a suitable value of k is chosen. One may say alternatively that the contours of equal q,p in h,k space are approximately parallel. Two such sets of contours (those for q_1 and p_{12} in pyrrole) are plotted in fig.15.2 - those for the other q's and p's are of similar shape. These show that we must not expect to be able to choose parameters 'h' and 'k' for a molecule on the basis of observed properties correlated solely with charge and bond order. In fig 15.2 we also give contours of total π-energy for this molecule. These cross the others at large angles and so if a quantity which can be correlated

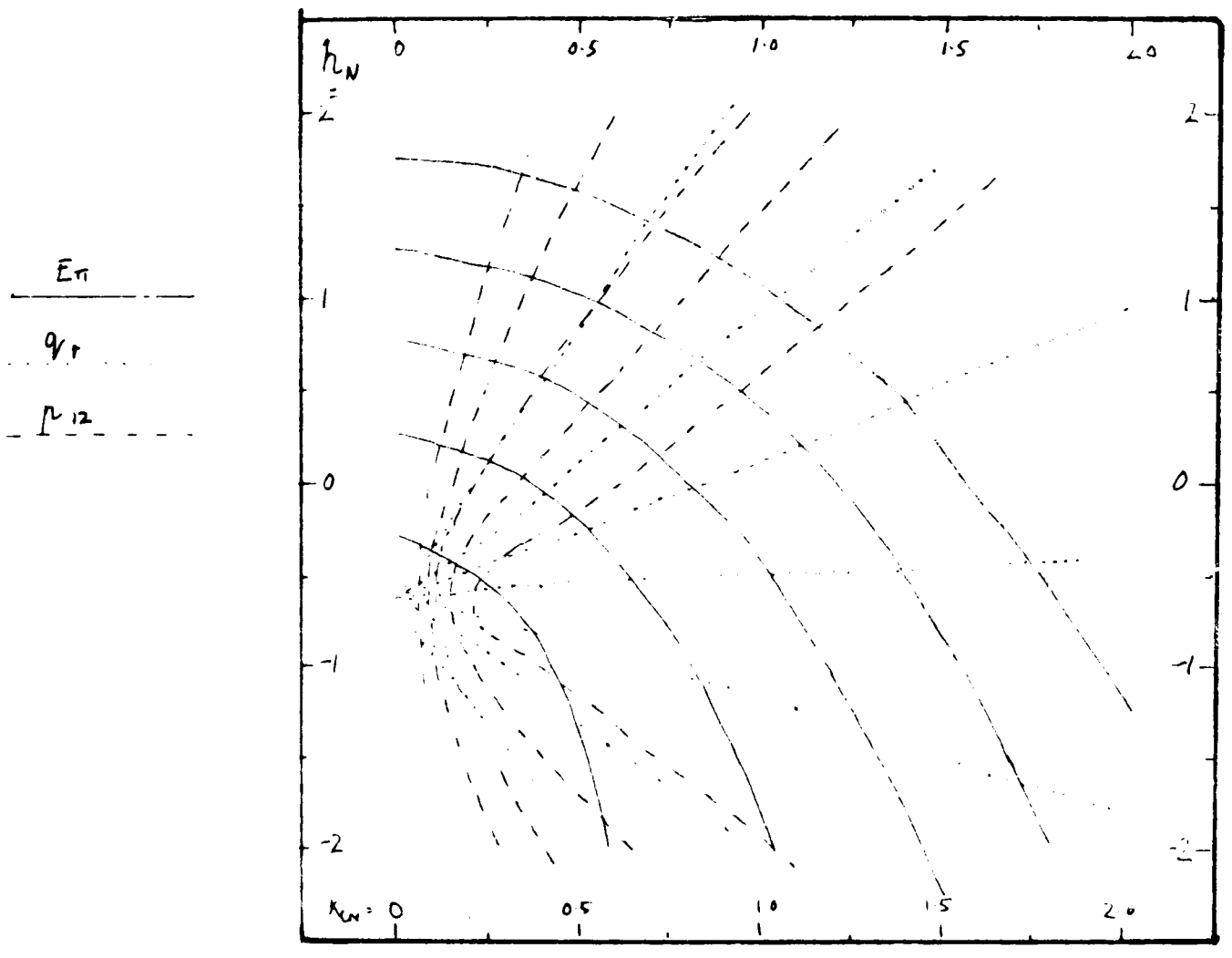


Fig 15.2 PYRROLE – CONTOURS OF EQUAL E_π, q_r, Γ FOR VARIATION OF h_N, k_{CN}.

with this energy (or an orbital energy which behaves similarly) is available as well as one correlated with charges and bond orders there is a chance of obtaining a good choice of h and k.

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CHAPTER II

A SELF-CONSISTENT HUCKEL MOLECULAR ORBITAL METHOD

1. The Method

The assumptions made in the HMO method when applied to hydrocarbons usually include taking all atom parameters h_r equal (and this value may be arbitrarily taken as zero) and all the bond parameters k_{rs} equal (and this value is taken as unity so that the energy unit is the standard resonance integral β_o).

In general for non-alternant hydrocarbons these assumptions lead to different π-electron densities (charges) and π-bond orders around the molecule, and it is in this respect that the results may be said not to be self-consistent. If algebraic relations, usually empirical with some theoretical justification, between the parameters h_r and k_{rs} on the one hand and q_r and p_{rs} on the other, are chosen, a set of q_r and p_{rs} which, when used to define h_r and k_{rs} for a second calculation, reproduces the same q_r and p_{rs} is said to be <u>self-consistent</u>. The present method of calculating such quantities, together with the self consistent energy parameters and any other quantities derived from MO theory, will be called the <u>SCHMO</u> method.

In outline the SCHMO method consists of calculating a set of q_r and p_{rs} by the HMO method (the <u>zero-order calculation</u>); using the empirical relations to derive the h_r and k_{rs} for a second HMO calculation (the first iteration); using the results of this to start a second iteration and proceeding in this way until (if ever) a self-consistent set of q_r and p_{rs} is produced. The empirical relations used for hydrocarbons in the present work are:

$$h_r^{(j)} = w(1 - q_r^{(j-1)}) \qquad (1.1)$$

$$k_{rs}^{(j)} = \exp\{-(\ell_{rs}^{(j-1)} - \ell_b)/a\} \qquad (1.2)$$

$$\ell_{rs}^{(j-1)} = \ell_o - g p_{rs}^{(j-1)}$$

Bracketed superscripts indicate iteration numbers. Equation (1.1) was first used by Wheland and Mann (1949) with w = 1, but is now associated with the name of Streitwieser (1959,60) who recommends the value of 1.4 for w. (for best reproduction of experimental ionization energies). The quantity $(1 - q_r)$ is the excess of positive charge at atom r. h_r which measures the power of nucleus r to attract the π-electrons should thus be expected to be monotonically related to this excess and might be expected to resemble the ionization potential of the atom for an excess of +1 ($q_r = 0$) and the electron affinity for $q_r = 2$. (Both quantities to be divided by our energy unit β). The use of a linear formula is only justifiable on account of its simplicity and is reliable only for small deviations of q_r from unity. More elaborate formulae have been proposed by Pritchard and Sumner (1956) and by Brown and Heffernan (1960). It would be a simple matter to modify the programmes to be described in this thesis to use any formulae one might desire.

In (1.2) ℓ represents bond length, ℓ_b being the length of our standard bond, the C-C bond in benzene for which k is 1. The linear relation between bond length and bond order may be chosen to fit any two known bonds, the usual ones being the benzene bond and a hypothetical single bond between two trigonally hybridized carbon atoms. The constant a may be chosen to fit experimental data obtained from studies of the vibrational spectrum. Formulae like (1.2) relating bond parameter (or resonance integral) and

bond order have been used by several workers. The numerical values of the constants used in most of the present work are those proposed by Coulson and Golębiewski (1961).

Self consistent calculations using formulae like (1.1) and a linear version of (1.2) have been done on desk machines by Muller, Pickett and Mulliken (1954) and more recently on a computer by Ehrenson (1961) who included the effect of not neglecting overlap between adjacent atomic π-orbitals.

Formula (1.1) may be extended to heteroatoms if we introduce two new quantities h_r^o and n_r^o . h_r^o is the atom parameter of the Hückel theory and represents the difference in electron-attracting power between the atom r and the standard carbon atom. n_r^o is the number of π-electrons provided by atom r for conjugation; it thus usually has the value 1, but for atoms such as the nitrogen in pyrrole is 2. The net positive charge is now $(n_r^o - q_r)$ and (1.1) becomes:

$$h_r^{(j)} = h_r^o + w(n_r^o - q_r^{(j-1)}) \qquad (1.3)$$

In order properly to allow for heterobonds it would be necessary to use different bond order/length relationships for different types of bond. Since such relationships are not readily available they have not been incorporated into the programme. To do so, however, would not be difficult - it would also be possible to use different values of w for different atoms. The general version of (1.2) used in the programmes now to be described is

$$k_{rs}^{(j)} = k_{rs}^o \exp\{-B(0.12 - 0.18p_{rs}^{(j-1)})\} \qquad (1.4)$$

k_{rs}^o is the bond parameter of the Hückel theory. The constants w and B may be specified as part of the programme data, usual values being 1.4 and 2.683 respectively. (If B is set to zero, no correction for bond-order variation is made at all - some calculations of this sort have been done).

2. Convergence of the method

No systematic study of the convergence of this sort of method has been made, although Ehrenson (1962) has shown that, in certain circumstances which he defines, the w-technique, when applied to a certain class of symmetrical molecules with no more than two sorts of π-electron centre, will necessarily give divergent results.

Experience with the present programmes on non-alternant hydrocarbons has shown that, especially with the smaller molecules such as fulvene, an oscillatory divergence usually occurs. A well-known extrapolation method* used to accelerate the convergence of iterative methods is to assume that each q_r, $p_{r,s}$ is approaching its self-consistent value in such a way that the differences between the values at succeeding iterations and the self-consistent value are in geometric progression. If R is the common ratio of this progression and succeeding iterations for a particular q_r or $p_{r,s}$, whose self-consistent value is x, are $x^{(j-2)}$, $x^{(j-1)}$, $x^{(j)}$ we have:

$$\frac{x^{(j)} - x}{x^{(j-1)} - x} = \frac{x^{(j-1)} - x}{x^{(j-2)} - x} = R \qquad (2.1)$$

and so:

$$x = \frac{x^{(j-1)}\{x^{(j-1)} - x^{(j-2)}\}x^{(j)}}{2x^{(j-1)} - x^{(j-2)} - x^{(j)}} \qquad (2.2)$$

These formulae have the great advantage for computer use that they cover the cases when the series $x^{(j-2)}$, $x^{(j-1)}$, $x^{(j)}$ is converging towards x ($|R| < 1$) or diverging away from x($|R| > 1$), and also include the case when succeeding iterations oscillate on either side of x($R < 0$) as well as when they tend monotonically towards x ($R > 0$).

---

* see e.g. Modern Computing Methods, HMSO (1961) p. 123.

In the present method the calculated charges and bond orders from three successive iterations are each treated by formula (2.2). As the convergence is not exactly in geometric progression this does not give self-consistent values, but it is found in practice for non-alternant hydrocarbons that the set of $p_{r,s}$ and q_r so generated, when used to derive new $k_{r,s}$ and h_r by means of (1.3) and (1.4), gives a series of three iterations which converge, or at the very worst show greatly reduced divergence. Further application of (2.2) after further sets of three iterations then rapidly gives self-consistent answers.

However although this method gave results for the molecule fulvene which were self-consistent to within an average of 0.0003 in the q_r and $p_{r,s}$ at the 10th iteration, examination of the separate iterations showed that at certain stages jumps in the wrong direction occurred. The reason for this is that if three succeeding estimates of a $p_{r,s}$ or q_r are approximately in arithmetic progression the denominator of (2.2) becomes very small and an erroneous estimate of the self-consistent value is thereby made.

For the non-alternant hydrocarbons for which this method was developed it is found that succeeding estimates of $p_{r,s}$ and q_r tend to oscillate rather than to vary monotonically; thus a series of iterations in approximate arithmetic progression is likely to occur only for a particular $p_{r,s}$ or q_r which has nearly attained its self-consistent value. If in these circumstances we take $x = x^{(j-1)}$ we should retain the symmetry in $x^{(j-2)}$, $x^{(j)}$ and would be making a reasonable estimate of the self-consistent value. For sake of simplicity the programme has been written to use this estimate of x for any particular $p_{r,s}$ or q_r which is varying monotonically rather

than oscillating. This criterion is not, however, satisfactory for alternant hydrocarbons where only the bond orders are not self-consistent as for these the convergence is monotonic; but, since these usually converge rapidly, extrapolation procedures may usually be omitted.

The extrapolation procedure described will be called <u>improvement</u>, and the set of x's will be called the <u>improved estimates</u> of the p_{rs} and q_r. The improvement formula being non-linear the improved estimates of the q_r will not necessarily add up to the total number of electrons, as do the set of charges derived from a solution of the secular equations. In order to make them do this, and hence to keep constant the sum $\sum_r h_r$, the quantity $(G - \sum_r q_r)/N$ is added to each q_r where G is the number of π-electrons, N the number of π-centres. The term 'improvement' will henceforth be assumed to include this correction.

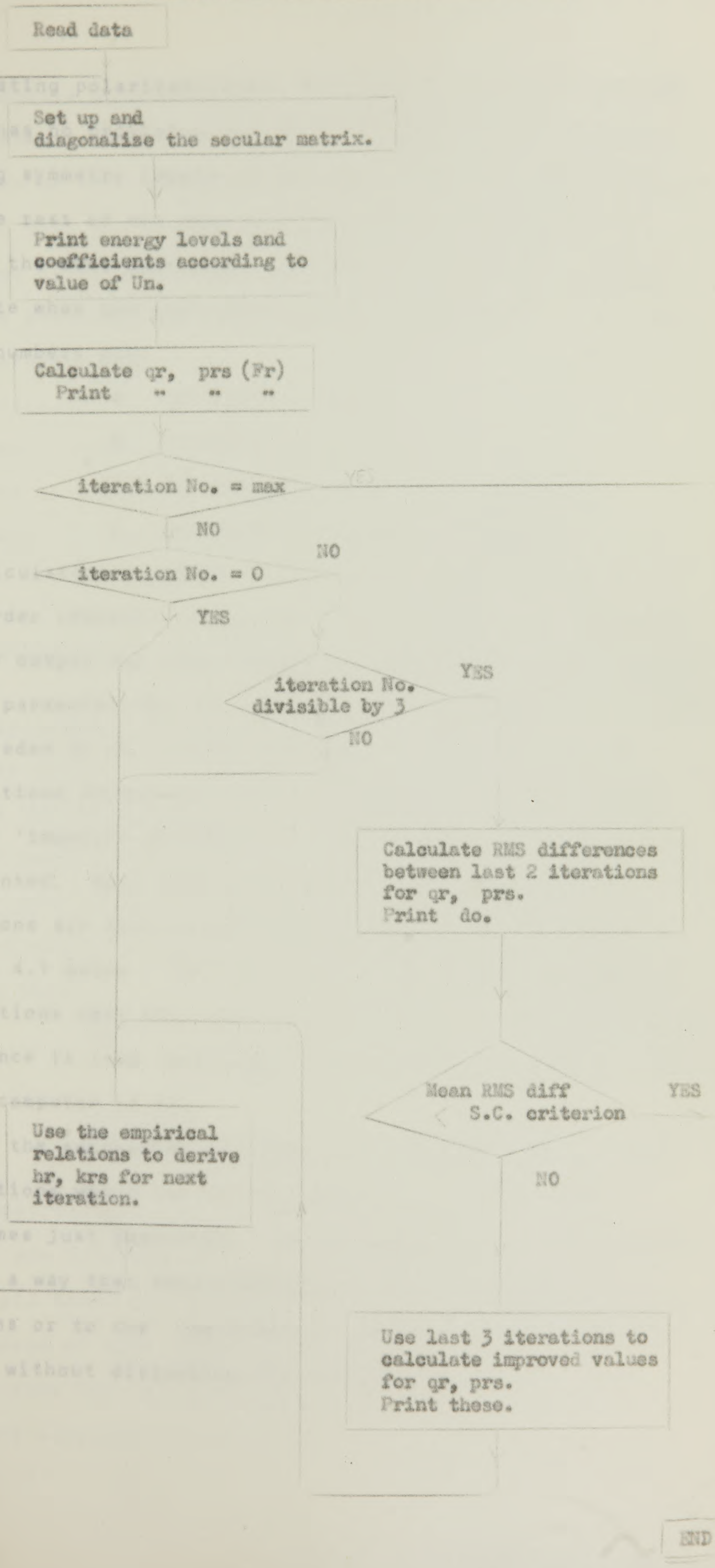
3. <u>The SCHMO Programmes</u>

Two main versions of the programme have been written. The first of these (1/4.5) is for molecules with C_{2v} or C_{2h} symmetry. The second (1/4.6) is for molecules with no symmetry. Molecules with D_{2h} or higher symmetry may be treated by 1/4.5 if the higher symmetry is ignored. Programme 1/4.5 is based on Chapters 0-3 of HMO Programme C. Programme 1/4.6 resembles HMO Programme H as far as data structure is concerned but is somewhat different in detail. Both programmes will accept heteroatoms for each of which must be given the two numbers n_r^o and h_r^o (equation (1.3)). The general logical arrangement of the programmes is given in Flow chart II.1. There are some minor differences in the behaviour of the two programmes.

The layout of the data resembles that of the HMO programmes closely except that there is no provision for

Flow chart II.1

Outline flow diagram for SCHNO Programmes



calculating polarizabilities and so Xn, Yn, Zn are omitted. 1/4.6 has no provision for selected atoms or bonds or for quoting symmetry labels on orbitals. Between the heading and the rest of the data must be given four numbers, to define the semi-empirical relations (1.3) and (1.4) and to indicate when the calculation is to be stopped.

These numbers are:

w	constant in (1.3)
B	constant in (1.4)
T	The maximum number of iterations.
Z	The self-consistency criterion.

The calculation proceeds automatically starting with a zero-order (Hückel) calculation implicitly called iteration 0. The output for each iteration corresponds to the values of the parameters Un, Vn, Wn (see Appendix A to chapter I) and is preceded by the iteration number. After each set of 3 iterations beyond the first an 'improvement' is carried out and 'improved estimates' of the charges and bond orders are printed. Root mean square deviations between two iterations are also calculated and printed as explained in Section 4.1 below. The calculation is ended when <u>either</u> (i) T iterations have been done <u>or</u> (ii) the mean root mean square difference is less than Z <u>or</u> (iii) Handswitch 9 on the console of the computer is set.

In the succeeding sections are described some of the calculations which led to the particular form of the programmes just described. The programmes have been written in such a way that modifications to the semi-empirical relations or to the 'improvement' formulae may be made if desired without disturbing the overall logic.

3.1 Results Obtained with the SCHMO Programmes

The greatest amount of computation done with the programmes has been on non-alternant hydrocarbons, and it was with these in mind that the programmes were devised - some of the results of these calculations are presented and discussed in section 4. The programmes may also be used, however, for alternant hydrocarbons where a wide range of bond-orders in the zero-order calculation may make a self-consistent calculation necessary. Some work on cyclobutadiene derivatives is reported in section 5. Finally the application of the programmes to heterosystems is briefly discussed in section 6.

4. Application of the SCHMO Programmes to non-alternant hydrocarbons

4.1 Development of the method of extrapolation

The measure of degree of self-consistency which has been used is the Root-mean-square Difference calculated from the sets of bond orders and charges at two successive iterations. For any pair of iterations j-1 and j two numbers may be computed which we shall call $\overline{\Delta p}^{(j)}$ and $\overline{\Delta q}^{(j)}$. They are defined thus:

$$\overline{\Delta_p}^{(j)} = \left\{\frac{1}{H} \sum_{\substack{\text{bonds} \\ r-s}} (p_{rs}^{(j)} - p_{rs}^{(j-1)})^2\right\}^{\frac{1}{2}} \quad (4.1)$$

$$\overline{\Delta_q}^{(j)} = \left\{\frac{1}{F} \sum_{\substack{\text{atoms} \\ r}} (q_r^{(j)} - q_r^{(j-1)})^2\right\}^{\frac{1}{2}} \quad (4.2)$$

The summations are over those bonds and atoms for which the results are tabulated (the 'selected' bonds and atoms in 1/4.5; all bonds and atoms in 1/4.6). H and F are respectively the numbers of such bonds and atoms.

To show how the convergence is improved by using different extrapolation methods we give in Table II.1 the

results for the molecules fulvene and azulene:

(a) with no 'improvement' (straight iterations)

(b) using formula (2.2) on all $p_{r,s}$ and q_r every third iteration.

(c) full 'improvement' technique carried out every third iteration.

In the calculations (b) and (c) improvement was carried out on sets of 3 orbitals including the zero-order calculation (first improvement) or the previous improved estimates (succeeding improvements). A slightly better rate of convergence is obtained for fewer improvements if three iterations beyond the zeroth and beyond the improved estimates are carried out before the next improvement. In this method the three sets of results used for improvement are all derived from solutions of the secular equations, whereas in (b) and (c) only the two latter ones are. The programmes in their present form use this technique. When tried on fulvene this gave $\overline{\Delta_p}^{(9)} = 0.00000$, $\overline{\Delta q}^{(9)} = 0.00009$; a little better than (c) for one fewer improvement.

Table II.1 shows clearly the divergence of (a) (individual $p_{r,s}$, q_r diverge oscillatorily) and, especially for azulene, the erratic results obtained with (b). Here certain of the $p_{r,s}$ and q_r sometimes occur approximately in arithmetic progression and so are wrongly improved by equation (2.2). The calculations reported in section 4.3 all used extrapolation method (c) and so were not done with programme 1/4.5 in its final form.

TABLE II.1

IMPROVEMENT OF EXTRAPOLATION PROCEDURE

Fulvene

(a)			(b)			(c)		
j	$\overline{\Delta p}^{(j)}$	$\overline{\Delta q}^{(j)}$	j	$\overline{\Delta p}^{(j)}$	$\overline{\Delta q}^{(j)}$	j	$\overline{\Delta p}^{(j)}$	$\overline{\Delta q}^{(j)}$
3	0.0505	0.3283	2	0.01151	0.2811	3	0.05050	0.32836
5	0.1834	0.4392	4	0.01457	0.1099	5	0.00433	0.01325
7	0.2202	0.5757	6	0.00103	0.02456	7	0.00059	0.00051
9	0.0796	0.7206	8	0.00008	0.00355	9	0.00013	0.00006
			10	0.00002	0.00031	12	0.00000	0.00005
			12	0.00006	0.00072			
			14	0.00004	0.00018			
			16	0.00000	0.00014			

Azulene

(a)			(b)			(c)		
j	$\overline{\Delta p}^{(j)}$	$\overline{\Delta q}^{(j)}$	j	$\overline{\Delta p}^{(j)}$	$\overline{\Delta q}^{(j)}$	j	$\overline{\Delta p}^{(j)}$	$\overline{\Delta q}^{(j)}$
3	0.00977	0.0426	3	0.00977	0.04260	3	0.00977	0.04260
5	0.00269	0.1692	5	0.00016	0.00342	5	0.00016	0.00342
			7	0.00004	0.00011	7	0.00001	0.00012
			9	0.00237	0.01233	9	0.00000	0.00001
			11	0.00036	0.00157			
			13	0.00143	0.00819			
			15	0.00021	0.00101			

4.2 The value of w

The value of w was chosen as 1.4 by Streitwieser and Nair (1959) to reproduce ionization potentials of hydrocarbons and so there is no guarantee that it is the best value to use for predicting bond orders and charges. Consequently calculations were done for fulvene with w = 1.0, 1.4, and 1.8. The results of these are given in Table II.2.

It will be seen that the variation with w in this range is small compared with the difference between HMO and SCHMO results. On account of the crudity of the method anyway there seems likely to be no strong reason for choosing any value other than the usual 1.4. This has been done for all other calculations on hydrocarbons reported below.

TABLE II.2

FULVENE: CHARGES AND BOND ORDERS. VARIATION OF w

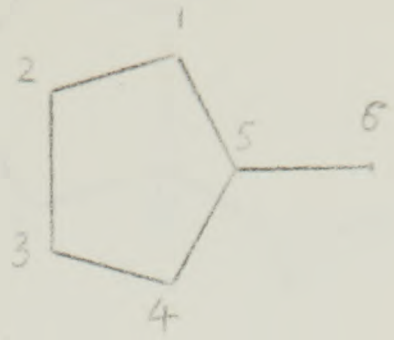
	w=1.0	w=1.4	w=1.8	HMO
p_{aa}	0.39760	0.39163	0.38683	0.52024
p_{12}	0.86268	0.86590	0.86841	0.77794
p_{56}	0.86736	0.87169	0.87489	0.75863
p_{15}	0.34955	0.34475	0.34107	0.44910
q_1	1.04410	1.04124	1.03880	1.09233
q_2	1.03134	1.02860	1.02654	1.07303
q_5	0.99103	0.98451	0.98032	1.04699
q_6	0.85809	0.87582	0.88899	0.62229

4.3 Results for nine non-alternant hydrocarbons

The accompanying tables give the final iteration as produced by the computer programme. The iteration number gives an idea of the rate of convergence. The criterion for stopping the calculation was that $\frac{1}{2}\{\overline{\Delta_p}^{(j)} + \overline{\Delta_q}^{(j)}\} \leqslant 0.00005$, the results tabulated being those of the $(j + 1)$th iteration. Results self-consistent to 3 figures were obtained when j was about half its final value. The time of computation on Mercury varied from 5 minutes for fulvene to 18 minutes for heptalene

Comparison of the results with experiment is not simple because of the difficulty of obtaining sufficiently reliable experimental data. Features of the results which are worth

FULVENE



ENERGY

	S=0	
1	2.0339121	B1-SZ
2	1.0589446	B1-SZ
3	0.6949164	A2-AZ
4	-0.3450926	B1-SZ
5	-1.6683035	A2-AZ
6	-1.7743771	B1-SZ

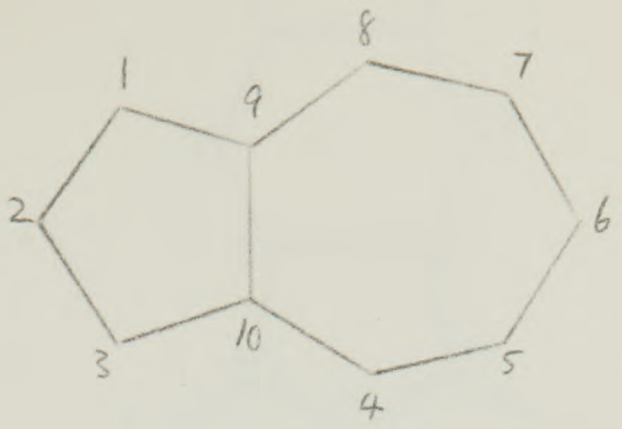
TOTAL PI ENERGY
7.5755462

COEFFICIENTS

	1	2	3	4	5	6
E	2.03391	1.05894	0.69492	-0.34509	-1.66830	-1.77438
	B1-SZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
1	0.41376	0.09309	0.58374	-0.35665	-0.39905	-0.43925
2	0.38015	0.45885	0.39905	0.33258	0.58374	0.18530
5	0.52206	-0.46873	0.00000	-0.30804	0.00000	0.64254
6	0.30988	-0.58471	0.00000	0.65536	0.00000	-0.36413

BOND ORDERS			CHARGES		FREE VALENCES	
2	3	0.39163	1	1.04124	1	0.52140
1	2	0.86590	2	1.02860	2	0.47453
5	6	0.87169	5	0.98451	5	0.17086
1	5	0.34475	6	0.87582	6	0.86036

AZULENE



ITERATION 10

ENERGY

	S=o	
1	2.2009152	B1-SZ
2	1.6413456	B1-SZ
3	1.4063184	A2-AZ
4	0.8275849	B1-SZ
5	0.4175592	A2-AZ
6	-0.3532412	B1-SZ
7	-0.7093208	A2-AZ
8	-1.5999655	B1-SZ
9	-1.8530888	B1-SZ
10	-1.9781066	A2-AZ

TOTAL PI ENERGY
12.9874466

COEFFICIENTS

	1	2	3	4	5	6
E	2.20092	1.64135	1.40632	0.82758	0.41756	-0.35324
	B1-SZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
1	0.28541	-0.30020	0.18542	-0.25676	0.52784	-0.05032
7	0.25976	0.40048	0.36058	-0.13765	-0.33596	0.11329
8	0.32438	0.13890	0.49923	0.26128	-0.13126	0.44571
9	0.42947	-0.19119	0.29389	0.33185	0.30214	-0.32944
2	0.25108	-0.35120	0.00000	-0.57731	0.00000	0.33494
6	0.24444	0.51377	0.00000	-0.37440	0.00000	-0.49266

	7	8	9	10
E	-0.70932	-1.59997	-1.85309	-1.97811
	A2-AZ	B1-SZ	B1-SZ	A2-AZ
1	-0.32561	0.34509	-0.37533	-0.28458
7	-0.48059	0.38195	0.30736	0.16169
8	0.35658	-0.18476	-0.27280	-0.32617
9	0.18936	-0.06497	0.23692	0.53524
2	0.00000	-0.44331	0.41428	0.00000
6	0.00000	-0.44365	-0.31078	0.00000

BOND ORDERS

9	10	0.30692
1	9	0.61748
7	8	0.65607
8	9	0.61304
1	2	0.65065
7	6	0.64157

CHARGES

1	1.10101
7	0.97939
8	0.91849
9	1.01756
2	1.03934
6	0.92776

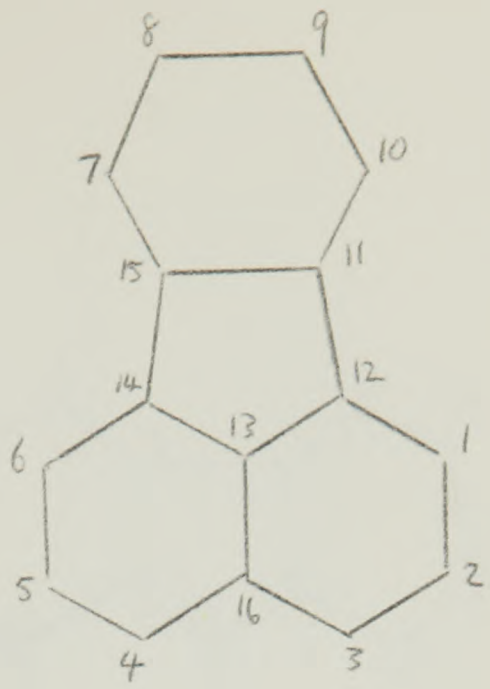
FLUORANTHENE ITERATION 12

83c

ENERGY

S=o

1	2.4175659	B1-SZ
2	1.9573346	B1-SZ
3	1.6933066	A2-AZ
4	1.4166879	B1-SZ
5	1.1116651	A2-AZ
6	0.9632813	B1-SZ
7	0.7441760	B1-SZ
8	0.6479690	A2-AZ
9	-0.4167435	A2-AZ
10	-0.9155189	B1-SZ
11	-0.9541056	B1-SZ
12	-1.1839385	A2-AZ
13	-1.4227811	B1-SZ
14	-1.6055344	A2-AZ
15	-2.1822002	A2-AZ
16	-2.2711623	B1-SZ



TOTAL PI ENERGY

21.9039728

COEFFICIENTS

	1	2	3	4	5	6
E	2.41757	1.95733	1.69331	1.41669	1.11167	0.96328
	B1-SZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
1	0.21467	-0.10650	0.41266	0.10513	0.03145	0.40268
2	0.16540	-0.20086	0.37962	-0.15595	0.24280	0.38818
3	0.18567	-0.27990	0.23506	-0.31095	0.23062	-0.01554
9	0.13104	0.32448	0.03855	-0.40762	-0.21896	0.02165
10	0.18697	0.31422	0.10336	-0.17521	-0.46018	-0.00047
11	0.32603	0.29429	0.13868	0.16384	-0.29676	-0.02258
12	0.34764	-0.31097	0.31456	0.29201	-0.19772	-0.00007
13	0.37501	-0.17873	0.00000	0.18388	0.00000	-0.41856
16	0.29150	-0.35564	0.00000	-0.29004	0.00000	-0.44351

	7	8	9	10	11	12
E	0.74418	0.64797	-0.41674	-0.91552	-0.95411	-1.18394
	B1-SZ	A2-AZ	A2-AZ	B1-SZ	B1-SZ	A2-AZ
1	-0.17026	-0.23904	-0.33853	0.19050	0.36734	-0.09239
2	0.07830	0.21610	-0.16186	-0.02449	-0.39502	0.29675
3	0.21476	0.35737	0.38144	-0.15585	0.02326	-0.25455
9	-0.35271	0.19847	-0.20279	-0.27535	0.05516	-0.43005
10	0.08468	0.32544	-0.11745	0.52133	-0.10656	0.07960
11	0.42437	0.01177	0.25696	-0.20449	0.04712	0.34337
12	-0.19398	-0.35073	0.30456	-0.15512	0.01805	-0.17154
13	-0.36428	0.00000	0.00000	0.13153	-0.46254	0.00000
16	0.07885	0.00000	0.00000	0.18272	0.41127	0.00000

	13	14	15	16
E	-1.42278	-1.60553	-2.18220	-2.27116
	B1-SZ	A2-AZ	A2-AZ	B1-SZ
1	0.10151	-0.35359	-0.15305	0.24259
2	0.20830	0.35839	0.08683	-0.22613
3	-0.38187	-0.22780	-0.04075	0.27104
9	0.08592	0.32159	-0.28582	0.01639
10	-0.20608	-0.19458	0.33712	-0.05315
11	0.21062	-0.01058	-0.45664	0.10610
12	-0.34424	0.23077	0.25203	-0.33650
13	0.21712	0.00000	0.00000	0.45534
16	0.35831	0.00000	0.00000	-0.41302

BOND ORDERS

9	8	0.64934
11	15	0.58581
1	2	0.59223
1	12	0.69383
2	3	0.73733
9	10	0.67468
10	11	0.63080
11	12	0.34762
13	16	0.55292
3	16	0.53537
12	13	0.51344

CHARGES

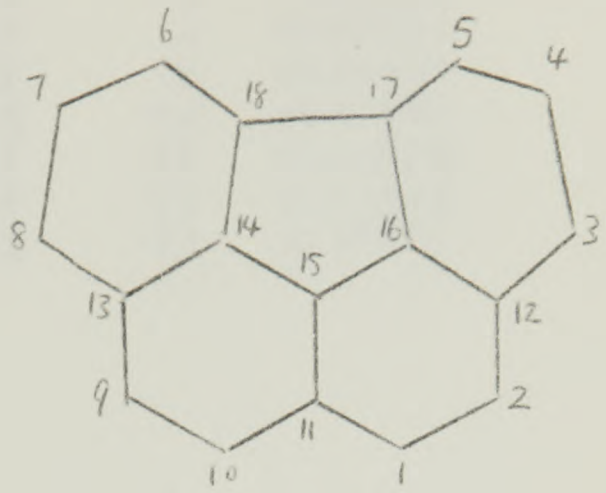
1	0.97607
2	0.99719
3	0.98407
9	1.00463
10	0.99986
11	1.01557
12	1.00985
13	1.02856
16	0.99699

BENZ-FLUORANTHENE

ITERATION 12

ENERGY

	S=0	
1	2.4701118	B1-SZ
2	2.0033789	A2-AZ
3	1.8571559	B1-SZ
4	1.4467021	B1-SZ
5	1.3555168	A2-AZ
6	1.1043094	B1-SZ
7	0.7647731	A2-AZ
8	0.7461653	B1-SZ
9	0.6604248	A2-AZ
10	-0.4187547	B1-SZ
11	-0.6978950	A2-AZ
12	-1.0151221	B1-SZ
13	-1.1609652	A2-AZ
14	-1.3150203	B1-SZ
15	-1.5492712	A2-AZ
16	-1.6708207	B1-SZ
17	-2.2348341	A2-AZ
18	-2.3458537	B1-SZ



TOTAL PI ENERGY
24.8170763

COEFFICIENTS

	1	2	3	4	5	6
E	2.47011	2.00338	1.85716	1.44670	1.35552	1.1043I
	B1-SZ	A2-AZ	B1-SZ	B1-SZ	A2-AZ	B1-SZ
1	0.17400	0.12746	0.34367	-0.05892	-0.28084	-0.29168
2	0.16933	0.24027	0.21722	-0.20989	-0.35795	-0.02391
12	0.25206	0.37359	0.03895	-0.25964	-0.19866	0.30891
3	0.15334	0.31153	-0.08618	-0.37911	0.10884	0.08935
4	0.13375	0.25819	-0.19085	-0.28896	0.32617	-0.19103
5	0.17786	0.20320	-0.27337	-0.03007	0.33961	-0.31091
17	0.30309	0.14988	-0.31341	0.23728	0.13365	-0.14883
16	0.33714	0.24288	-0.04753	0.18640	-0.04588	0.29140
11	0.27102	0.00000	0.44166	0.14949	0.00000	-0.32129
15	0.35278	0.00000	0.18216	0.33079	0.00000	0.19552

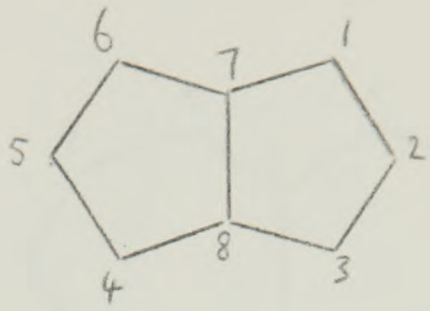
	7	8	9	10	11	12
E	0.76477	0.74617	0.66042	-0.41875	-0.69790	-1.01512
	A2-AZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
1	-0.21871	-0.11461	0.32550	-0.08915	0.40379	-0.14817
2	-0.15701	-0.35136	0.20168	0.28147	-0.26665	-0.17790
12	0.12441	-0.14794	-0.23429	-0.02954	-0.26022	0.37081
3	-0.21523	0.20072	-0.34147	-0.34512	0.15781	-0.09051
4	-0.27256	0.28010	0.00190	0.17319	0.13124	-0.25238
5	0.01256	0.00329	0.36107	0.28918	-0.26032	0.35847
17	0.27316	-0.26886	0.22640	-0.29533	0.06009	-0.12647
16	0.46546	0.02288	-0.01580	0.08593	0.29091	-0.13449
11	0.00000	0.31240	0.00000	-0.28353	0.00000	0.36880
15	0.00000	0.44981	0.00000	0.29808	0.00000	-0.11331

	13	14	15	16	17	18
E	-1.16097	-1.31502	-1.54927	-1.67082	-2.23483	-2.34585
	A2-AZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
1	0.15015	0.28393	-0.24693	0.29115	0.06732	-0.23377
2	-0.16468	-0.29610	0.36117	-0.10470	-0.14195	0.21575
12	0.03715	0.10038	-0.32958	-0.14451	0.26998	-0.28441
3	0.34959	-0.20666	0.19046	0.28322	-0.21164	0.16382
4	-0.43510	0.17500	0.01467	-0.33165	0.21425	-0.11374
5	0.15043	-0.01860	-0.22402	0.27072	-0.26882	0.10146
17	0.24386	-0.14466	0.33658	-0.13550	0.39678	-0.12913
16	-0.23523	0.35249	-0.00093	0.07240	-0.28642	0.33005
11	0.00000	-0.06512	0.00000	-0.40849	0.00000	0.34759
15	0.00000	-0.44869	0.00000	0.16038	0.00000	-0.40454

BOND ORDERS			CHARGES		FREE VALENCES	
17	18	0.34924	1	0.99793	1	0.44624
1	2	0.78972	2	0.99025	2	0.45368
2	12	0.48864	12	0.99836	12	0.11852
12	3	0.55924	3	0.98951	3	0.45361
12	16	0.56564	4	1.00021	4	0.40192
3	4	0.71920	5	0.98219	5	0.44341
4	5	0.61093	17	1.01405	17	0.17383
5	17	0.67771	16	1.02821	16	0.15674
17	16	0.53126	11	0.98336	11	0.13345
11	15	0.60643	15	1.01523	15	0.16880
1	11	0.49609				
16	15	0.47841				

PENTALENE

ITERATION 16



ENERGY

	S=o	
1	2.1981419	B1-SZ
2	1.4334029	B1-SZ
3	0.9573521	A2-AZ
4	0.3498510	B1-SZ
5	0.1554847	A2-AZ
6	-1.3919692	B1-SZ
7	-1.7391413	B1-SZ
8	-1.9631220	A2-AZ

TOTAL PI ENERGY
9.8774957

COEFFICIENTS

	1	2	3	4	5	6
E	2.19814	1.43340	0.95735	0.34985	0.15548	-1.39197
	B1-SZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
6	0.33711	-0.37003	0.42586	0.11199	-0.50000	0.33627
7	0.43432	0.00000	0.37052	-0.49438	0.00000	-0.00000
1	0.33711	0.37003	0.42586	0.11199	0.50000	-0.33627
2	0.28995	0.47555	0.00000	0.48011	0.00000	0.52331
5	0.28995	-0.47555	0.00000	0.48011	0.00000	-0.52331

	7	8
E	-1.73914	-1.96312
	B1-SZ	A2-AZ
6	-0.35187	-0.26200
7	0.25876	0.60226
1	-0.35187	-0.26200
2	0.43061	0.00000
5	0.43060	0.00000

BOND ORDERS

7	8	0.59152
6	7	0.49768
7	1	0.49768
6	5	0.65497
1	2	0.65497

CHARGES

6	0.88894
7	1.14066
1	0.88894
2	1.08146
5	1.08146

FREE VALENCES

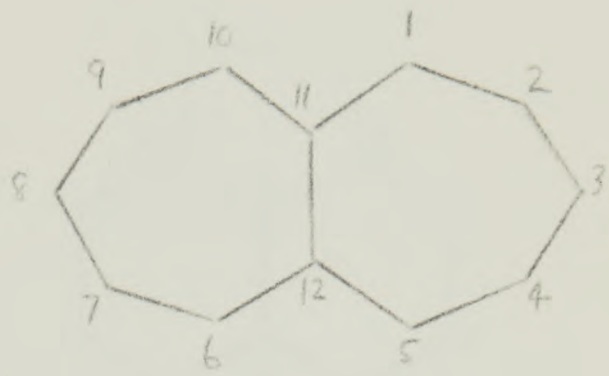
6	0.57940
7	0.14518
1	0.57940
2	0.42210
5	0.42210

HEPTALENE

ITERATION 16

ENERGY

	S=o	
1	2.2078200	B1-SZ
2	1.6986577	B1-SZ
3	1.4308603	A2-AZ
4	1.2875232	B1-SZ
5	1.0058640	A2-AZ
6	-0.0928276	B1-SZ
7	-0.2458508	A2-AZ
8	-0.6738047	B1-SZ
9	-1.0225299	A2-AZ
10	-1.7193900	B1-SZ
11	-1.8615441	B1-SZ
12	-2.0147779	A2-AZ



TOTAL PI ENERGY
15.0757953

COEFFICIENTS

	1	2	3	4	5	6
E	2.20782	1.69866	1.43086	1.28752	1.00586	-0.09283
	B1-SZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
9	0.21709	-0.36217	0.27041	-0.29502	-0.36762	0.00088
10	0.28198	-0.20461	0.36298	0.04464	-0.33890	-0.40294
11	0.46167	0.00000	0.30040	0.38744	0.00000	0.00000
1	0.28198	0.20461	0.36298	0.04464	0.33891	0.40294
2	0.21709	0.36217	0.27041	-0.29502	0.36762	-0.00088
3	0.18322	0.39235	0.00000	-0.41452	0.00000	-0.41865
8	0.18322	-0.39235	0.00000	-0.41452	0.00000	0.41865

	7	8	9	10	11	12
E	-0.24585	-0.67380	-1.02253	-1.71939	-1.86154	-2.01478
	A2-AZ	B1-SZ	A2-AZ	B1-SZ	B1-SZ	A2-AZ
9	-0.39085	0.12310	0.33891	-0.34472	-0.31730	-0.15528
10	0.12366	0.30828	-0.36762	0.21394	0.27103	0.32086
11	0.40483	-0.32763	-0.00000	0.00000	-0.17148	-0.49586
1	0.12366	0.30828	0.36762	-0.21394	0.27103	0.32086
2	-0.39085	0.12310	-0.33890	0.34472	-0.31730	-0.15528
3	0.00000	-0.41506	0.00000	-0.41327	0.34975	0.00000
8	0.00000	-0.41506	0.00000	0.41327	0.34975	0.00000

BOND ORDERS

11	12	0.54602
9	10	0.68908
10	11	0.51304
11	1	0.51304
1	2	0.68908
9	8	0.60907
2	3	0.60907

CHARGES

9	0.94721
10	1.06470
11	0.90698
1	1.06470
2	0.94721
3	1.06921
8	1.06921

FREE VALENCES

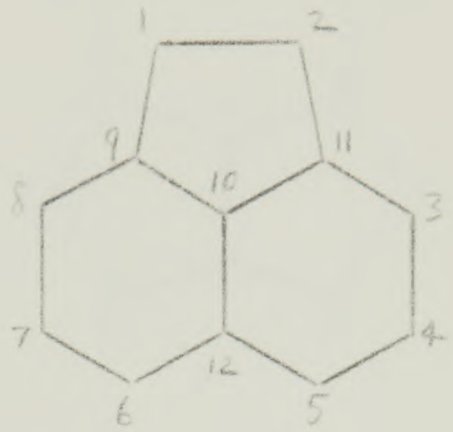
9	0.43390
10	0.52993
11	0.15995
1	0.52993
2	0.43390
3	0.51392
8	0.51392

ACENAPHTHYLENE

ITERATION 12

ENERGY

	S=o	
1	2.3415963	B1-SZ
2	1.6796517	A2-AZ
3	1.6315307	B1-SZ
4	0.9692709	B1-SZ
5	0.8050873	A2-AZ
6	0.6897244	B1-SZ
7	-0.3489206	A2-AZ
8	-0.9509085	B1-SZ
9	-1.3216257	A2-AZ
10	-1.3545971	B1-SZ
11	-1.8791519	A2-AZ
12	-2.2616533	B1-SZ



TOTAL PI ENERGY
16.2337227

COEFFICIENTS

	1	2	3	4	5	6
E	2.34160	1.67965	1.63153	0.96927	0.80509	0.68972
	B1-SZ	A2-AZ	B1-SZ	B1-SZ	A2-AZ	B1-SZ
2	0.24024	0.09182	0.39404	0.04193	0.18898	0.50804
11	0.35659	0.29772	0.26362	-0.00383	0.42294	-0.20951
3	0.24558	0.42330	0.03306	-0.41032	0.18397	-0.19232
4	0.20858	0.40027	-0.22119	-0.38350	-0.29882	0.09262
5	0.24156	0.25206	-0.37862	0.02653	-0.40282	0.24102
10	0.41694	0.00000	0.06431	0.40315	0.00000	-0.42943
12	0.36344	0.00000	-0.39948	0.44905	0.00000	0.06534

	7	8	9	10	11	12
E	-0.34892	-0.95091	-1.32163	-1.35460	-1.87915	-2.26165
	A2-AZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
2	0.31806	-0.01201	0.39475	-0.13876	0.44595	0.08805
11	0.29039	0.02757	-0.08048	0.38294	-0.37640	-0.33471
3	-0.36866	-0.40086	-0.23726	-0.12200	0.30784	0.24015
4	-0.14829	0.38915	0.42235	-0.22141	-0.22388	-0.22684
5	0.39574	0.01424	-0.32098	0.40570	0.12068	0.27331
10	0.00000	0.42003	0.00000	-0.28737	0.00000	0.46484
12	0.00000	-0.44396	0.00000	-0.35863	0.00000	-0.42035

BOND ORDERS

2	1	0.85741
2	11	0.38041
11	3	0.68397
3	4	0.59584
4	5	0.73509
10	12	0.55763
11	10	0.50811
5	12	0.53341

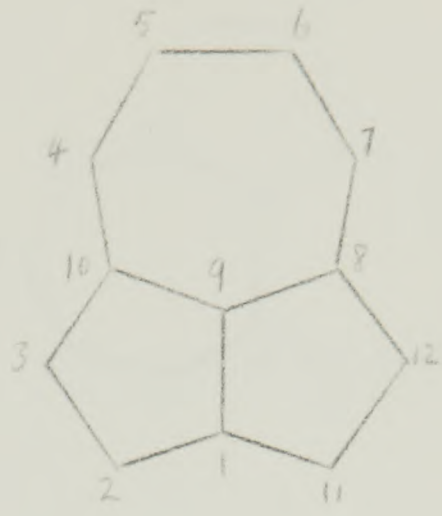
CHARGES

2	1.03398
11	1.01616
3	0.95956
4	0.99518
5	0.97261
10	1.04982
12	0.99517

FREE VALENCES

2	0.49423
11	0.15956
3	0.45225
4	0.40112
5	0.46354
10	0.15820
12	0.10759

1.8-PENTENO-AZULENE



ITERATION 14

ENERGY

	S=o	
1	2.3203573	B1-SZ
2	1.7215015	B1-SZ
3	1.6590381	A2-AZ
4	0.9050287	B1-SZ
5	0.8924437	A2-AZ
6	0.4006604	B1-SZ
7	-0.2615858	A2-AZ
8	-0.5469638	B1-SZ
9	-1.3098931	A2-AZ
10	-1.8164502	A2-AZ
11	-1.8963978	B1-SZ
12	-2.0677385	B1-SZ

TOTAL PI ENERGY
15.7980597

COEFFICIENTS

	1	2	3	4	5	6
E	2.32036	1.72150	1.65904	0.90503	0.89244	0.40066
	B1-SZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
6	0.20692	0.48969	0.13728	0.32713	-0.21767	-0.09632
7	0.25786	0.31154	0.35808	-0.06395	-0.39780	0.06831
8	0.36919	0.01982	0.42227	-0.37546	-0.09639	0.11522
12	0.24385	-0.14471	0.35228	0.05252	0.34437	0.46135
11	0.24170	-0.26691	0.22476	0.37280	0.40804	0.12263
1	0.33515	-0.33932	0.00000	0.31256	0.00000	-0.48639
9	0.40086	-0.16125	0.00000	-0.33863	0.00000	-0.50321

	7	8	9	10	11	12
E	-0.26159	-0.54696	-1.30989	-1.81645	-1.89640	-2.06774
	A2-AZ	B1-SZ	A2-AZ	A2-AZ	B1-SZ	B1-SZ
6	-0.34274	-0.30814	0.39961	0.39575	0.04660	-0.06302
7	-0.22347	0.51598	-0.16617	-0.36876	-0.14208	0.20314
8	0.42504	-0.03968	-0.15706	0.32722	0.24256	-0.38555
12	0.09277	-0.23196	0.41700	-0.27352	-0.37405	0.10133
11	-0.37858	0.13009	-0.33785	0.15974	0.42273	0.14388
1	0.00000	0.19355	0.00000	0.00000	-0.44758	-0.44775
9	0.00000	-0.30912	0.00000	0.00000	0.00743	0.59145

BOND ORDERS

6	5	0.66536
6	7	0.62833
7	8	0.64561
8	12	0.47232
12	11	0.78683
1	9	0.65595
8	9	0.42793
11	1	0.45690

CHARGES

6	0.93027
7	0.91755
8	0.95708
12	1.07740
11	1.00138
1	1.12347
9	1.10916

FREE VALENCES

6	0.43836
7	0.45811
8	0.18619
12	0.47290
11	0.48833
1	0.16231
9	0.22024

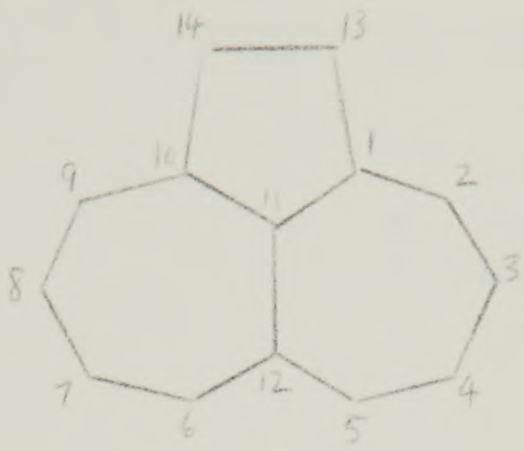
1.10-PENTENO-HEPTALENE

ITERATION 14

ENERGY

S=0

1	2.3190651	B1-SZ
2	1.7600646	A2-AZ
3	1.7094385	B1-SZ
4	1.3358661	B1-SZ
5	1.1100584	A2-AZ
6	0.7039171	B1-SZ
7	0.2370651	A2-AZ
8	-0.2982412	B1-SZ
9	-0.7422155	A2-AZ
10	-0.7472912	B1-SZ
11	-1.5036370	A2-AZ
12	-1.8576514	B1-SZ
13	-1.9506762	A2-AZ
14	-2.0757613	B1-SZ



TOTAL PI ENERGY

18.3509495

COEFFICIENTS

	1	2	3	4	5	6
E	2.31907	1.76006	1.70944	1.33587	1.11006	0.70392
	B1-SZ	A2-AZ	B1-SZ	B1-SZ	A2-AZ	B1-SZ
13	0.22788	0.07456	-0.33888	-0.03576	0.15965	0.51709
1	0.33704	0.21908	-0.29021	-0.01698	0.36312	-0.08821
2	0.21590	0.36189	-0.10670	0.33801	0.30524	-0.23385
3	0.16784	0.39250	0.08812	0.42468	-0.01565	-0.06451
4	0.17970	0.34508	0.28435	0.23972	-0.36284	0.21303
5	0.23510	0.20579	0.36389	-0.08821	-0.34290	0.18413
11	0.43727	0.00000	-0.10443	-0.33574	0.00000	-0.40351
12	0.39121	0.00000	0.35513	-0.40550	0.00000	-0.10295

	7	8	9	10	11	12
E	0.23707	-0.29824	-0.74222	-0.74729	-1.50364	-1.85765
	A2-AZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
13	0.27829	-0.10796	-0.28436	0.17585	-0.33811	0.06911
1	0.38483	0.12892	-0.10882	-0.29064	0.13355	-0.19259
2	-0.15717	-0.34690	0.37873	-0.19847	0.15512	0.26947
3	-0.36431	0.00788	-0.19747	0.41061	-0.35065	-0.32643
4	0.07581	0.38835	-0.27320	-0.09758	0.38506	0.34204
5	0.33360	-0.14570	0.38760	-0.28641	-0.26936	-0.34129
11	0.00000	0.44561	0.00000	0.22369	0.00000	0.02638
12	0.00000	-0.39998	0.00000	0.34654	0.00000	0.30048

	13	14
E	-1.95068	-2.07576
	A2-AZ	B1-SZ
13	0.44309	0.13121
1	-0.37732	-0.39488
2	0.28925	0.20179
3	-0.22590	-0.06580
4	0.14357	-0.08170
5	-0.07739	0.22558
11	0.00000	0.52253
12	0.00000	-0.41886

BOND ORDERS

13	14	0.65388
13	1	0.62310
1	2	0.49652
2	3	0.75998
3	4	0.51357
4	5	0.76905
11	12	0.62332
1	11	0.43796
5	12	0.47604

CHARGES

13	1.08784
1	1.06768
2	0.95154
3	1.01495
4	0.94495
5	1.00118
11	0.95531
12	0.90838

FREE VALENCES

13	0.45508
1	0.17448
2	0.47556
3	0.45850
4	0.44943
5	0.48697
11	0.23281
12	0.15666

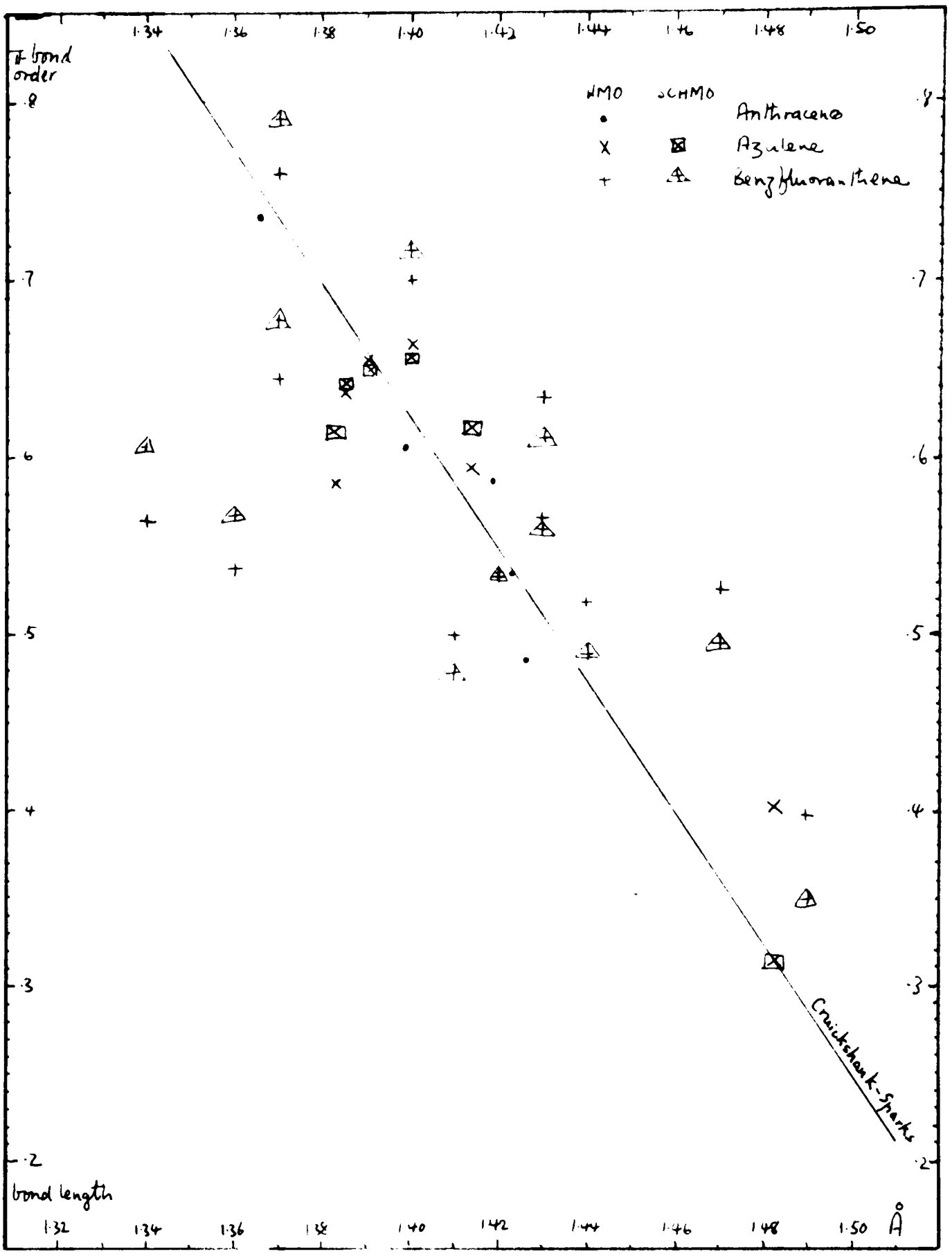


Fig 4·3

Comparison of Crystallographic Bond lengths with HMO and SCHMO π-bond orders

commenting on however are:

(a) Correlation of orbital energies and total π-energies with the known stability (and instability) of the molecules.

(b) Use of orbital coefficients to predict the shifts of electronic absorption bands in the UV Spectrum when inductive substituents are inserted into the systems.

(c) Correlation of bond orders with bond lengths observed by x-ray crystallography.

These will be considered below. The correlations of calculated π-dipole moment with the observed dipole moment of the molecule are of doubtful validity on account of the difficulty of taking correct account of the σ-electrons. The charge redistribution predicted by the SCHMO method is, however, a better approximation to the truth than that predicted by the HMO method, if only because some implicit account is taken of electronic repulsions.

(a) Total π-energy and orbital energies.

In table II.3 are given the delocalization energy (total π-energy less the energy of a Kekulé structure) and the energy of the highest occupied orbital. Both HMO and SCHMO results are given.

The interesting features of the table are that the DE calculated by the SCHMO method is less than that calculated by the HMO method for all molecules except fulvene, and that the numerical value of the energy of the top occupied orbital increases on iteration for all known molecules (except azulene) but decreases for the unknown molecules. For 1,10-penteno-heptalene of which only a derivative is known the HMO and SCHMO orbitals are almost equal. The DE (by both methods) also correlates with the stability if account is taken of the number of π-electrons and the fact that the existence of high occupied orbitals and low unoccupied orbitals leads to high reactivity.

TABLE II.3

Stability of non-alternant hydrocarbons

Molecule	π-electrons	DE HMO	DE SCHMO	m_r for top occ. MO HMO	m_r for top occ. MO SCHMO	Stability
Fulvene	6	1.466	1.576	0.618	0.695	known
Azulene	10	3.364	2.987	0.477	0.417	known
Fluoranthene	16	6.500	5.904	0.618	0.648	known
Benzfluoranthene	18	7.605	6.817	-	0.660	known
Pentalene	8	2.456	1.877	0.471	0.350	unknown
Heptalene	12	3.618	3.076	0.000	-0.093	unknown
Acenaphthylene	12	4.619	4.234	0.638	0.690	known
1.8-Pentenoazulene	12	4.366	3.798	0.480	0.401	*
1.10-Pentenoheptalene	14	4.911	4.351	0.241	0.237	*

* dimethyl derivative known

In particular the molecules pentalene and heptalene should be mentioned. Both of these are unknown compounds, both have non-bonding orbitals in the HMO approximation, but that in pentalene is unoccupied, whereas that in heptalene is occupied. In the SCHMO method the pentalene orbital becomes bonding while the heptalene one becomes anti-bonding, both of which facts predict even greater instability. (It is of interest to note that the tetra-aza-pentalenes described in I.14.2 may be said to owe their stability to the extra electrons provided by the nitrogens which will occupy these empty bonding orbitals).

(b) Substituent effects in the UV spectra.

The work on these systems was initiated when it was found (see Geuskens and Nasielski (1960)) that the shift of the lowest UV absorption band in fluoranthene on substitution by NH_3^+ in the 8-position was in the opposite direction to

that predicted from the coefficients of the orbitals in the HMO Method. Longuet-Higgins and Sowden (1952) showed that the first order term in the shift of the band due to an inductive substituent represented by a change in Coulomb term $\delta\alpha_r$ is given by:

$$\Delta E_{ab} = (c^2_{rb} - c^2_{ra})\delta\alpha_r$$

where a is the top occupied orbital and b the bottom unoccupied one.

The quantity $\delta\alpha_r$ for an electron-attracting group such as $-\overset{+}{N}H_3$ is negative and so a hypsochromic (to higher frequency) shift is to be expected for any position r where $|c_{ra}| > |c_{rb}|$. If we use HMO results the 2-,10- and 9- positions are predicted to show such a shift, whereas using SCHMO results only 2- and 10- should do so. Unfortunately Geuskens and Nasielski only prepared the 3- and 9- (=8-) compounds and observed a bathochromic shift in both cases. This is in accordance with the SCHMO prediction and it would be of great interest to know whether substitution in the 2- or 10-(=7-) positions would produce the predicted hypsochromic shift.

The predictions of shifts in substituted azulenes has been dealt with by several authors (Pullman etal (1950), Longuet-Higgins and Sowden (1952), Schulze and Heilbronner (1958)). All their interpretations with HMO results are equally valid using SCHMO results; it is only in the fluoranthene cases that different predictions occur.

(c) Bond orders and bond lengths.

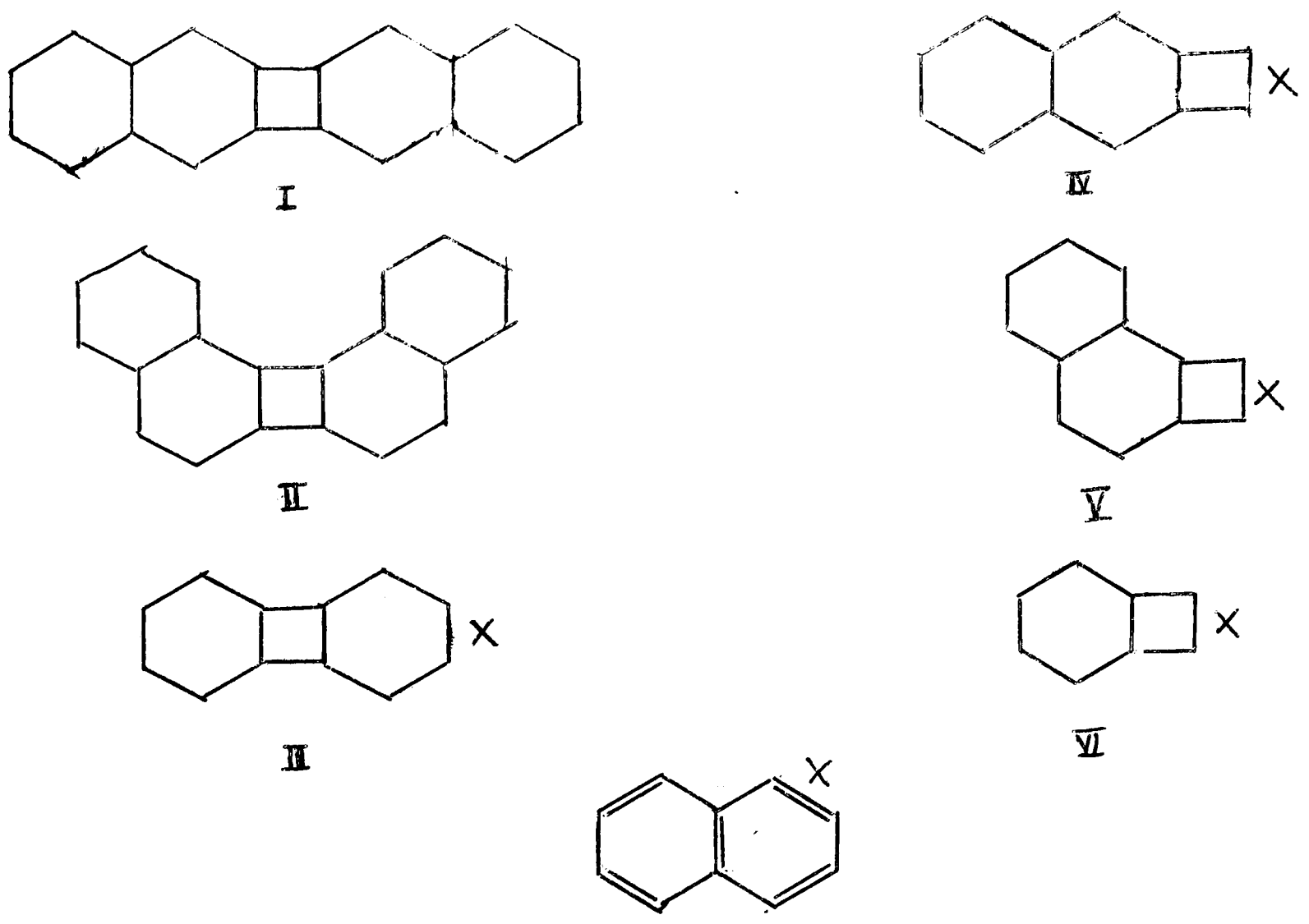
As far as can be ascertained the only molecules of the present series whose molecular structure has been determined by x-ray crystallography are azulene (Robertson etal (1962)) and benzfluoranthene (Ehrlich and Beevers (1956)).

The observed bond lengths are plotted against the bond orders calculated by the HMO and SCHMO methods in fig. 4.3. It will be seen that the SCHMO results are on average closer to the straight line corresponding to the formula of Cruickshank and Sparks (1960) than are the HMO results. Many of the lengths obtained by X-rays are in doubt by as much as 0.02Å and so it is difficult to say very much about the correlation.

4.4 General discussion of the SCHMO method for non-alternants

It is probably fair to say, that given a working programme and a computer on which to run it, it is worthwhile when considering a molecule of this class theoretically to start with an SCHMO calculation rather than the simple HMO. In no cases does it give inferior results and in certain cases where the redistribution of charge and allowance for varying bond lengths is significant, much better predictions may be made of several quantities observable experimentally.

5. Use of the SCHMO programmes for some calculations on cyclobutadiene derivatives



I II III IV V VI VII

Fig 5

A derivative of IV (with phenyl substituents in the 4-membered ring) has been synthesized by Cava, Hwang and van Meter (1963), and the present calculations are an attempt to predict the stability and chemical properties of this molecule in relation to the others of the series I-VI.

Ali and Coulson (1960) have treated I-III by the Hückel method and iterating to self consistency in the bond orders using a formula like (1.2). Their method necessitated a separate approach to the computer for each iteration, and so was somewhat time-consuming relative to a direct use of the SCHMO Programmes. When the charges

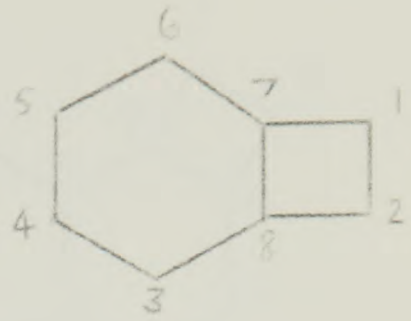
are all necessarily unity the convergence of the bond orders is found to be monotonic and so the 'improvement' procedure designed above for the oscillator convergence found in non-alternant systems is inapplicable (as mentioned in section 2 above.) However the rate of convergence is such that a sufficiently self-consistent set of bond orders is obtained by 3 straight iterations before the 'improvement' formulae are used - no modification of the programmes was thus required.

The results obtained for molecules IV-VI are shown in the accompanying tables.

Table II.4 collects together some of the more interesting quantities calculated by the HMO method and gives the corresponding results for diphenylene III and naphthalene VII. Corresponding quantities calculated by the SCHMO method for IV-VI are shown in table II.5. The only quantity (besides the bond orders) which is significantly changed on iteration is the energy of the lowest electronic transition (twice the energy of the top occupied orbital). The observed lowest absorption of IV (Cava et al 1963) is close to that of naphthalene VII and so, assuming VII to be not much changed on iteration (which is probable as the bond orders do not differ so greatly from the average) the SCHMO method gives a better prediction of this than the HMO.

The other quantities tabulated may be correlated with stability and chemical reactivity. IV is seen to have the greatest delocalization energy (excess π-energy over that for a suitable Kekulé structure), the highest localization energy for the fixation of two electrons at the ends of bond X (this quantity is a measure of

BENZ-CYCLOBUTADIENE



ITERATION 3

ENERGY

	S=0	S=0.25	
1	2.2356775	1.4341200	B1-SZ
2	1.4521654	1.0653861	B1-SZ
3	1.0575322	0.8364018	A2-AZ
4	0.4960243	0.4413004	B1-SZ

TOTAL PI ENERGY

10.4827988	7.5544167

COEFFICIENTS

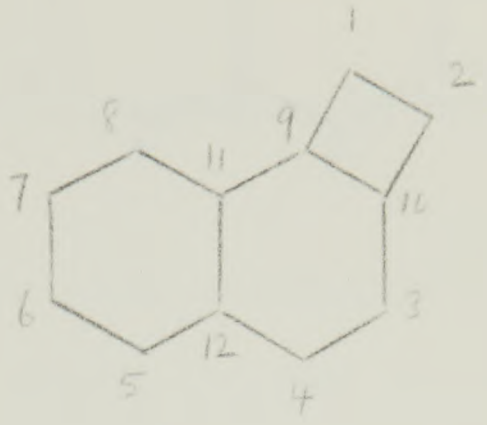
	1	2	3	4
E	2.23568	1.45217	1.05753	0.49602
	B1-SZ	B1-SZ	A2-AZ	B1-SZ
1	0.33290	-0.39950	0.11945	0.46402
7	0.46460	-0.15794	0.33549	-0.38294
6	0.32604	0.22402	0.55638	-0.18426
5	0.25888	0.51504	0.25223	0.32263

BOND ORDERS			CHARGES		FREE VALENCES	
1	2	0.94293	1	1.00000	1	0.62883
7	8	0.54980	7	1.00000	7	0.27533
5	4	0.74552	6	1.00000	6	0.42407
1	7	0.16029	5	1.00000	5	0.42519
7	6	0.74663				
6	5	0.56135				

R.M.S. DIFFERENCES

0.00034	0.00000

NAPHTHO(1,2)CYCLOBUTADIENE



ITERATION 3

ENERGY

	S=0	S=0.25
1	2.3379488	1.4755240
2	1.8532694	1.2664849
3	1.4183831	1.0470896
4	1.0903297	0.8567852
5	0.8880803	0.7267314
6	0.3695261	0.3382757

TOTAL PI ENERGY

15.9150751	11.4217814

COEFFICIENTS

	1	2	3	4	5	6
E	2.33795	1.85327	1.41838	1.09033	0.88808	0.36953
1	0.25513	-0.31473	0.25264	-0.19021	-0.30444	-0.37837
2	0.24556	-0.34288	0.17886	-0.30936	-0.15805	-0.41165
3	0.26659	-0.15736	-0.40064	-0.12205	0.47767	0.02434
4	0.25813	0.06613	-0.52336	0.02196	0.15109	-0.36302
5	0.21195	0.35789	-0.12668	-0.36464	-0.35431	0.22902
6	0.16453	0.37810	0.14095	-0.50976	0.00929	0.22397
7	0.17210	0.34504	0.35425	-0.18338	0.40492	-0.16805
8	0.23520	0.26965	0.35134	0.26535	0.33323	-0.25899
9	0.40630	-0.24443	0.19745	0.19193	-0.11462	0.43152
10	0.36661	-0.35723	-0.04812	-0.15485	0.27396	0.36964
11	0.39916	0.14770	0.13569	0.52228	-0.14119	0.08795
12	0.34808	0.28679	-0.35385	0.14933	-0.35011	-0.16279

BOND ORDERS

1	2	0.95694
1	9	0.13118
2	10	0.11269
3	4	0.65748
3	10	0.66398
4	12	0.60696
5	6	0.77243
5	12	0.50712
6	7	0.53662
7	8	0.77556
8	11	0.50028
9	10	0.65031
9	11	0.61450
11	12	0.49279

CHARGES

1	1.00000
2	1.00000
3	1.00000
4	1.00000
5	1.00000
6	1.00000
7	1.00000
8	1.00000
9	1.00000
10	1.00000
11	1.00000
12	1.00000

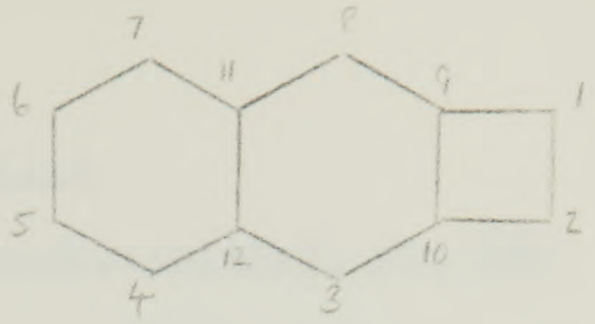
FREE VALENCES

1	0.64393
2	0.66242
3	0.41060
4	0.46761
5	0.45251
6	0.42300
7	0.41987
8	0.45621
9	0.33606
10	0.30507
11	0.12448
12	0.12518

R.M.S. DIFFERENCES

0.00252	0.00000

NAPHTHO(2,3)CYCLOBUTADIENE



ITERATION 3

ENERGY

	S=0	S=0.25	
1	2.3266244	1.4710052	B1-SZ
2	1.9119429	1.2936139	B1-SZ
3	1.3001201	0.9812005	A2-AZ
4	1.2216761	0.9358497	B1-SZ
5	0.7387754	0.6236003	A2-AZ
6	0.5228774	0.4624290	B1-SZ

TOTAL PI ENERGY

16.0440325 11.5353972

COEFFICIENTS

	1	2	3	4	5	6
E	2.32662	1.9119 4	1.3001 2	1.2216 8	0.7387 8	0.5228 8
	B1-SZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
1	0.24973	-0.33028	0.07689	0.31247	-0.12946	0.45633
9	0.37152	-0.32199	0.23043	0.03793	-0.29813	-0.33893
8	0.30908	-0.05702	0.41425	-0.22455	-0.35686	-0.22769
11	0.35706	0.26140	0.32421	-0.34957	0.06140	0.27036
7	0.22088	0.31402	0.36998	0.11159	0.44119	0.09282
6	0.16671	0.34212	0.16549	0.46460	0.26190	-0.20816

BOND ORDERS			CHARGES		FREE VALENCES	
1	2	0.90931	1	1.00000	1	0.59749
9	10	0.43209	9	1.00000	9	0.26733
11	12	0.56447	8	1.00000	8	0.47509
6	5	0.61608	11	1.00000	11	0.12984
1	9	0.22525	7	1.00000	7	0.43678
9	8	0.80738	6	1.00000	6	0.40886
8	11	0.44958				
11	7	0.58816				
7	6	0.70711				

R.M.S. DIFFERENCES

0.00181 0.00000

TABLE II.4

Stability of naphthocyclobutadienes, etc. HMO

Molecule:	III	IV	V	VI	VII
Total π-energy	16.506	16.200	15.996	10.381	13.683
Delocalization energy	4.506	4.200	3.996	2.381	3.683
Localization energy of bond x	1.35	0.52	0.32	0.38	1.26
Lowest electronic transition	0.890	0.679	0.295	0.525	1.236
Mean free valence of atoms joined by x	0.421	0.598	0.637	0.620	0.428

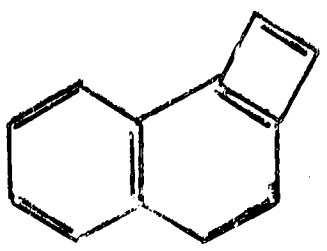
(Energy quantities in units of β_o)

Table II.5

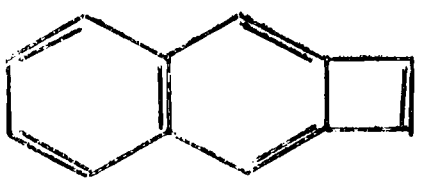
Stability of naphthocyclobutadienes, etc. SCHMO

Molecule:	IV	V	VI
Total π-energy	16.044	15.915	10.483
Delocalization energy	4.044	3.195	2.483
Lowest electronic transition	1.045	0.739	0.992
Mean free valence of atoms joined by X.	0.597	0.653	0.629

dienophile activity - the smaller the energy the more reactive the molecule) and the lowest free valence at the atoms joined by X. These facts all lead to a prediction of less stability for molecules V and VI. A similar qualitative conclusion may be drawn if Kekulé structures are drawn for IV and V starting with the dominant structure VII for naphthalene.



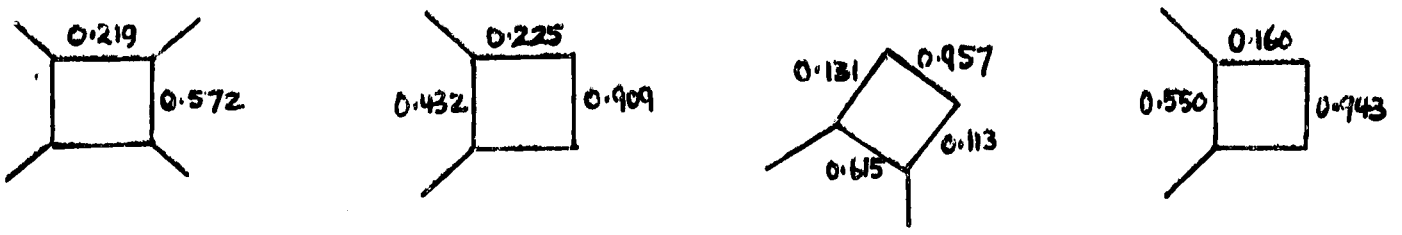
V



IV

V, where the degree of fixation would be greater, would be expected to be the less stable of the two.

That the double bonds X are practically fixed in this way is shown by the SCHMO bond orders which are extracted from the tables into Fig 5a. (Those for III are from Ali and Coulson 1960).



III IV V VI

Fig. 5a

The fixation is such that these molecules can only properly be described as an aromatic system and an isolated double bond (cf. I-III where a suitable description is two very weakly-interacting aromatic systems). A description as cyclobutadiene derivatives is not appropriate.

6. Application of the SCHMO method to heteromolecules

In order to apply the method to heteromolecules we need to modify the formulae (1.1) and (1.2). The revised form of (1.1) is given as (1.3) and has been used by Ehrenson (1962) in a full analysis of the w-technique applied to certain simple symmetrical systems. For all calculations described in sections 4 and 5, all h_r^o have been taken as zero and all n_r^o as 1. For heterosystems the choice of n_r^o is straightforward, but that of h_r^o is not, as one is faced with the same difficulties as in the choice of h_r in the HMO method. Equation 1.4 where an initial bond parameter k_{rs}^o is present as a factor on the right hand side but with different constants in the order-length relationship and a different value for B, is also applicable to heterobonds if suitable numerical values can be found. The proper choice of these as of k_{rs}^o and h_r^o is not simple and no attempts in this direction have been made in the present work.

However the programmes have been used by Dr. G. L. Caldow (1964) for some calculations on substituted benzenes using the w-formula only and making no correction for bond-length variation. Some of his calculations on fluorobenzenes and their cations in order to calculate ionization potentials brought up some further difficulties which have not been fully investigated. 1, 3, 5 - trifluorobenzene which retains the three-fold symmetry of the parent molecule has necessarily degenerate orbitals. The cation would thus presumably be distorted by the Jahn-Teller effect, but it is not obvious from which orbital an electron will be ionized. Since the two top

orbitals have different symmetries it is possible to get the computer to distinguish them and calculate self-consistent orbitals for the two 'different' ions. All that has been done, however, is to assume the electron ionized equally from the two orbitals; a procedure of somewhat doubtful validity.*

For 1, 2, 4-trifluorobenzene, where no such trouble would be expected, it is found that there are two orbitals which, while not degenerate, are related to a degenerate pair in benzene and have approximately opposite symmetries. These orbitals interchange in energy when fairly small changes are made in the values of h_F and h_C and so unless a lucky initial choice is made it is not possible automatically to approach a set of self-consistent orbitals by using the programme. Dr. Caldow has systematised the process of making a 'lucky initial choice', but unfortunately this is not possible on the computer. He is still working on these systems and it is possible that some method of treating these molecules may be devised.

---

* Dr. Caldow has since made some calculations where the top orbital is constrained to have a certain symmetry.

References - Chapter II

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CHAPTER III

THE ULTRA VIOLET SPECTRA OF BENZOLOGUES OF PYRENE

1. Introduction

The polynuclear aromatic hydrocarbons derived formally from pyrene by the addition of further benzene rings in various directions have been called benzologues of pyrene by Clar and others (cf. homologues) The formal process of addition of such rings to a molecule is called annelation by Clar (1952) and the direction perpendicular to the bond common to the new ring and the rest of the molecule is called the annelation axis or direction of annelation.

In his book (Clar 1952) Clar introduces the idea of an annelation effect, by which he means a shift towards the red (to lower frequency) of the chief bands in the ultraviolet absorption and fluorescence spectra as further rings are added to a molecule along any one annelation axis. (For introductions to the spectra of aromatic hydrocarbons and their interpretation see also e.g. Streitwieser (1961), Jaffé and Orchin (1962) or Murrell (1963)).

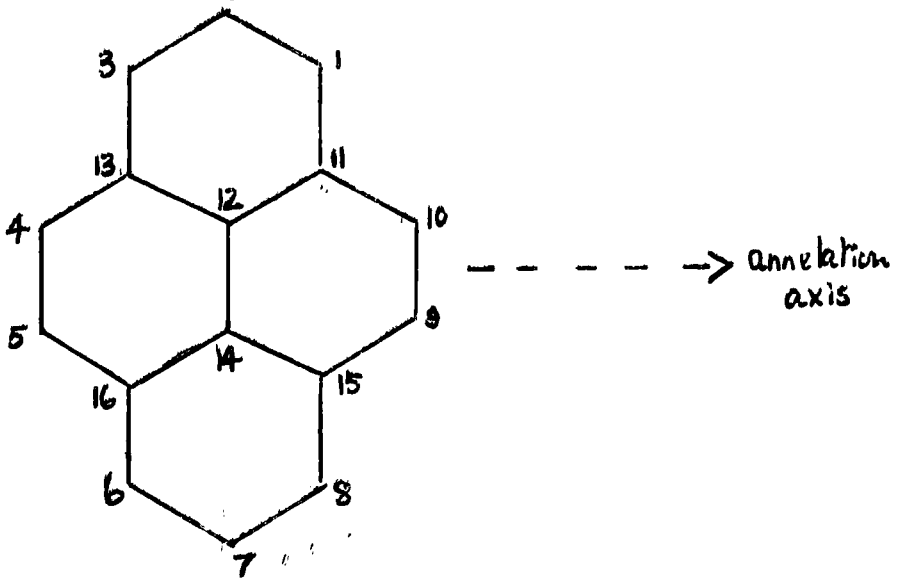
In a series of papers in Tetrahedron (Clar (1959a, b, c), (1960), (1961), (1962))* Clar has described what he calls asymmetric annelation effects in several series of aromatic hydrocarbons. The essence of these is that annelation on one side of the molecule causes the usual red shift for each additional ring, but that if rings are then added at the other side of the molecule, a much smaller and sometimes even a negative shift occurs in the spectrum.

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* Many of these results are discussed also in Clar's recent book 'Polycyclic Hydrocarbons'. (Clar 1964)

Clar's explanation of these asymmetric annelation effects involves such concepts as annelation at a fixed double bond, etc. which are difficult to understand fully, especially where they lead to asymmetrical pictures of symmetrical molecules.

The present work is an attempt to explain the asymmetric annelation effect in a set of benzologues of pyrene by considering the electronic transitions responsible for the UV-bands to be more or less localized in certain parts of the molecule. The justification for this approach is the low bond order predicted by the Hückel method for the bonds corresponding to bonds 4-13 etc. of pyrene.



Pyrene

1.1 Nomenclature of the molecules

In order to show their relation to pyrene the molecules will be referred to by symbolic names mPn where m is the number of rings to the left of the 4-5 pyrene bond and n the number to the right of the 9-10 bond. In this scheme pyrene itself is called 0P0, 4.5-benz-pyrene 1P0 or 0P1, etc. By an extension of the idea we may call phenanthrene

-1PO, triphenylene -1P1, etc.

2. Hückel Calculations

Hückel calculations, using the HMO programmes of Chapter I, have been done for $-1 \leqslant m \leqslant 3$ and $0 \leqslant n \leqslant 4$ (3P4 with 44 π-electrons is the largest molecule for which the programmes have been used). Bond orders, free valences and atom-atom self polarizabilities were calculated but in fig. 2 are shown only the bond-orders for the molecules OPO-OP5, together with the bond orders in the corresponding acenes

The results for the other molecules are not given as, apart from the bonds in the pyrene region, the bond orders may be predicted to within 0.001 by considering the following generalisations:

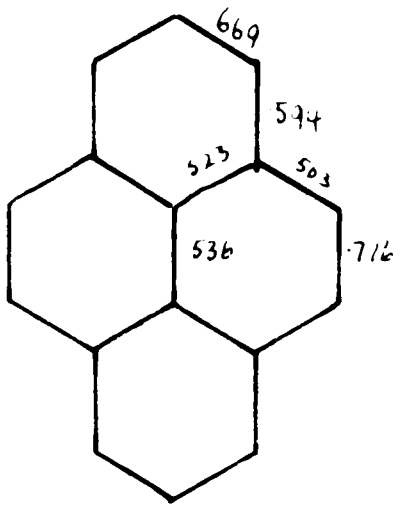
1. for $m \geqslant 2$ the bond derived from the 4-13 bond of pyrene has order 0.420

2. for $n \geqslant 2$ the bond derived from the 10-11 bond of pyrene has order 0.420

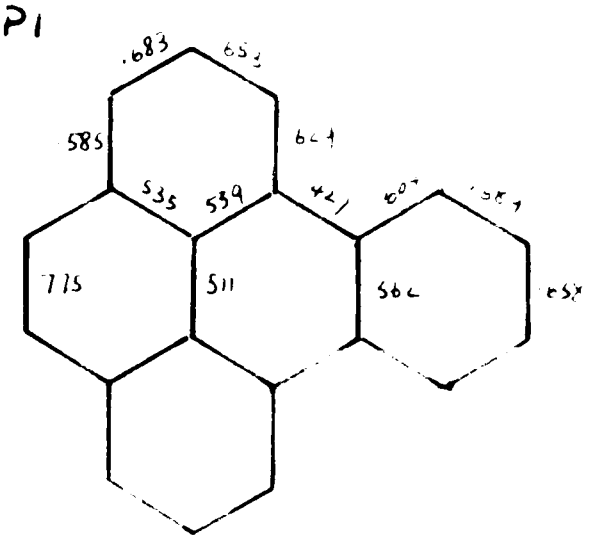
3. for $m \geqslant 2$ the bond orders in the left hand 'side chain' are independent of n, and vice versa.

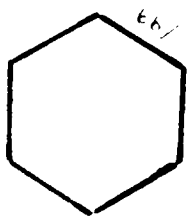
4. The central bond (derived from 12-14 in pyrene) has an order decreasing from .536 in OPO to .464 in 3P4. The bonds with order 0.420 ± 0.001 which are those of lowest order (and hence longest) will be referred to as the join bonds and the parts of the molecule joined by these bonds will be called the left, middle, and right fragments respectively. In most of the subsequent calculations we shall take $m \leqslant n$ and consider the middle fragment as fixed to and hence part of the left fragment.

OP0

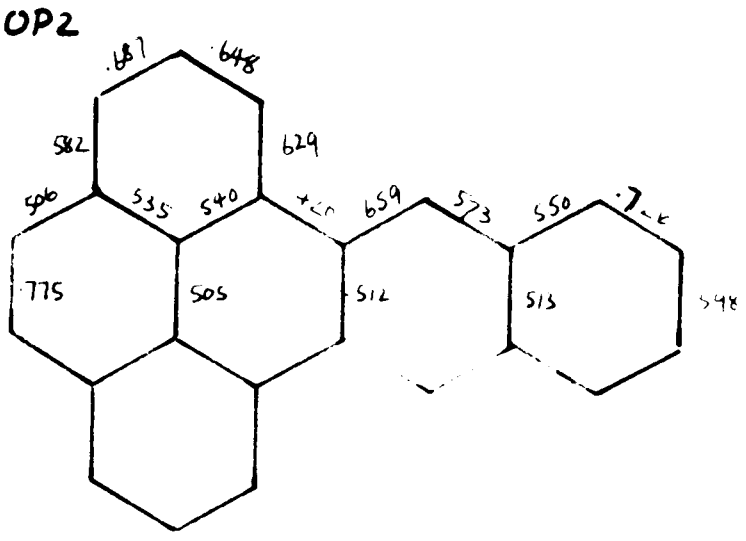


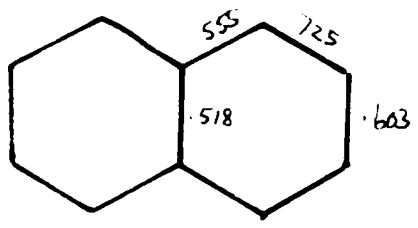
OP1



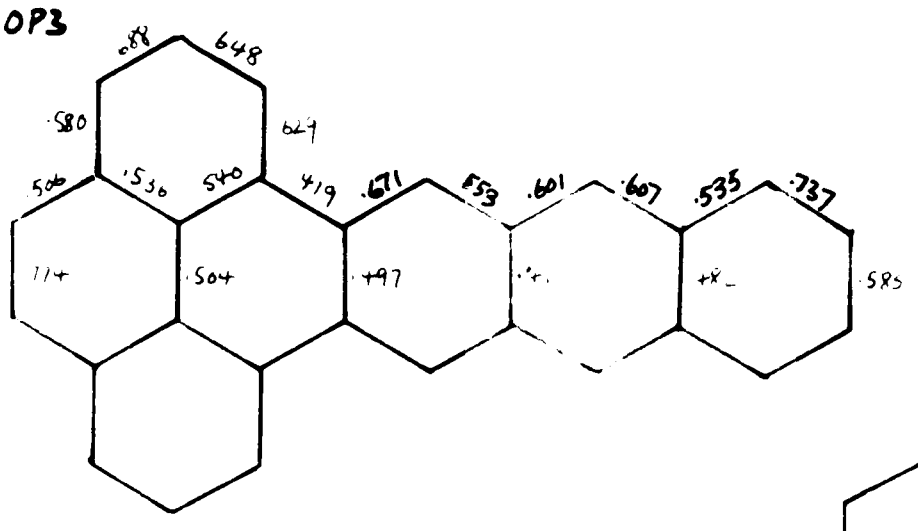


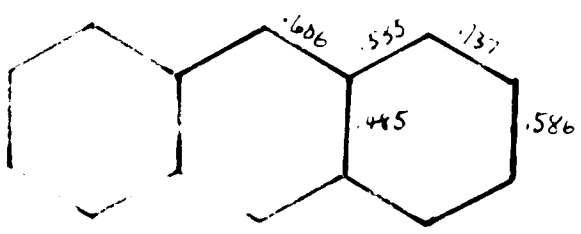
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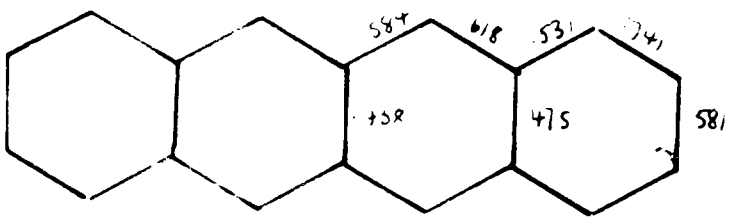




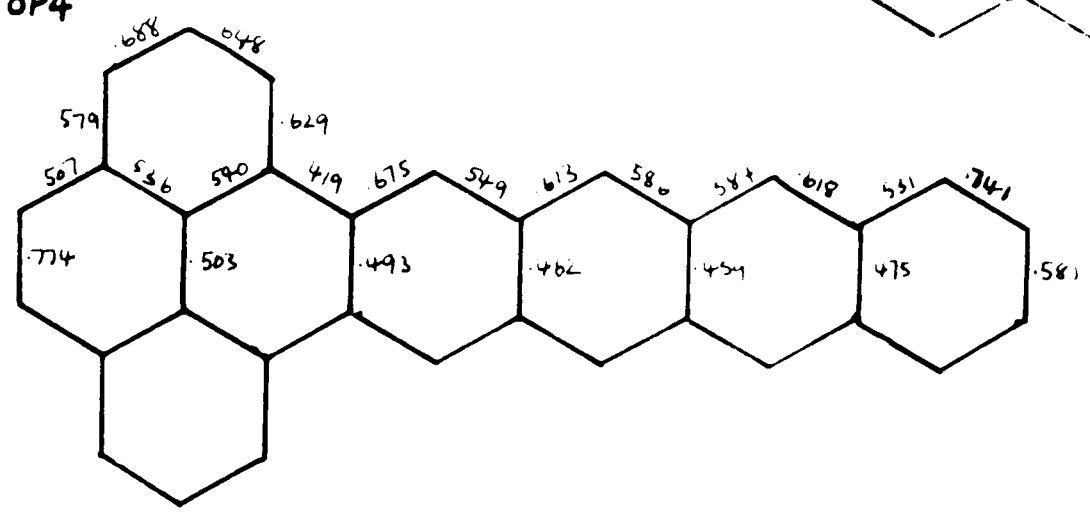
OP3



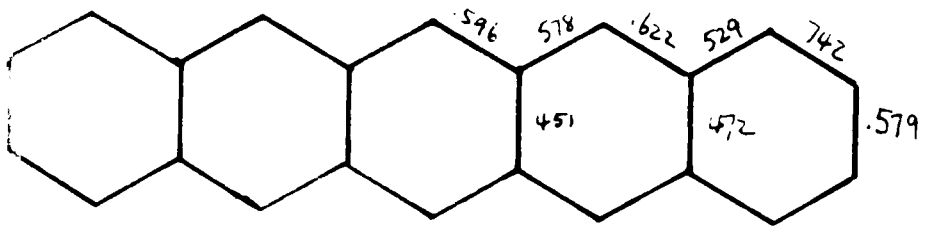




OP4



OP5



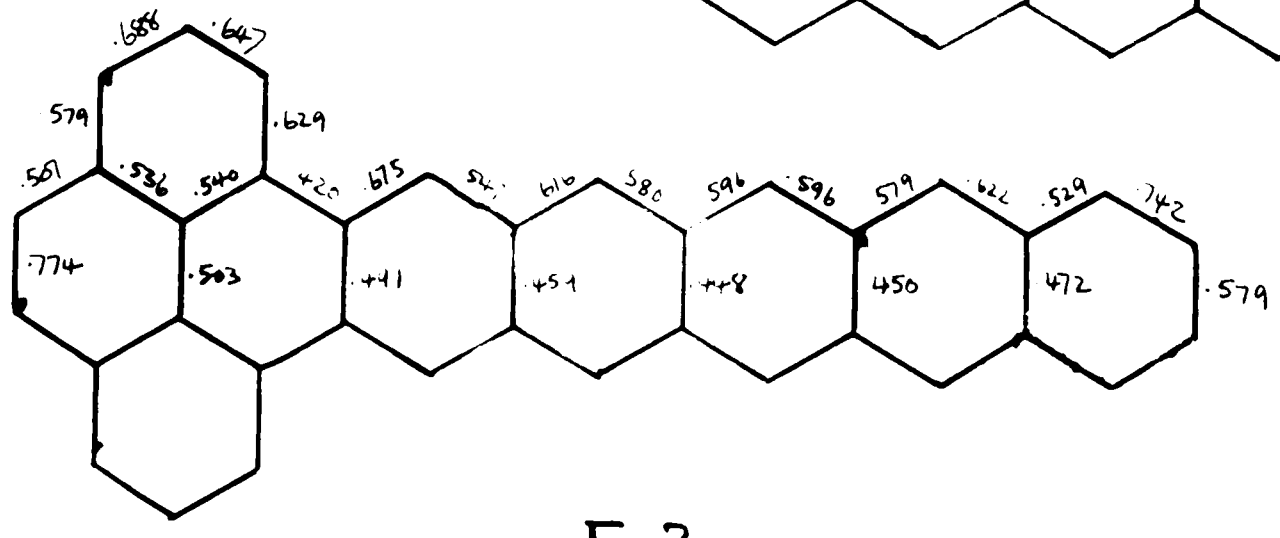


Fig 2 BOND ORDERS

2.1 Adjustment of β's according to bond orders

As well as the zero-order Hückel calculation just mentioned a further calculation was made using equation (1.4) of Chapter II to predict a value of β for each bond. This had the uniform effect of reducing the order of the join bond to 0.389 ± 0.001 and slightly enhancing the other differences from the benzene value. This calculation will be called the first iteration calculation.

2.2 HMO Energy levels and coefficients

Further justification for our consideration of the molecule as made up from 'fragments' comes from a study of the symmetries, energy parameters, and MO coefficients of the top occupied orbitals of the molecules. The p-band (in Clar's nomenclature) of the spectrum has been associated by Dewar and Longuet-Higgins (1954) with the transition involving the jump of one electron from the top occupied orbital to the bottom unoccupied orbital. Since these orbitals are complementary (see I.6) they have opposite symmetry with respect to that symmetry plane which passes through no atoms (for D_{2h} molecules) and the transition dipole will be perpendicular to this direction. For those molecules where this has been possible this polarization of the p-band is confirmed experimentally. (see e.g. Murrell 1963).

For molecules with m or n $\geq$ 3 the top occupied orbital is seen to approximate very closely to that of the corresponding polyacene. For the smaller molecules, on the other hand, the top orbital is more evenly spread over the molecule. The lowest Hückel transition energy (twice the energy parameter for the top occupied orbital) is in the range 1.1 $\longrightarrow$ 0.9 β

for all molecules with $n \leqslant 2$, $m \leqslant n$, but for $n \leqslant 2$, $m = 3$ it drops to about 0.7β and for $n \leqslant 2$, $m = 4$ to about 0.5β. Similar drops in the observed p-band occur in all cases where these have been studied (Clar 1963).

All these facts are in favour of a treatment of these molecules as built up from two or three 'fragments', the transitions of the combined molecule being related to those of both fragments if these have similar energies but to only one if it has a much lower transition than the other.

To do this in such a way that we can use experimental information about the transitions in the fragments, we consider configurations built up from Hückel orbitals of the fragments. These configurations will be of two types: locally excited configurations and charge transfer configurations. These configurations are allowed to interact as in the work of Longuet-Higgins and Murrell (1955) on the spectra of diphenyl and styrene. These calculations are described in section 3.

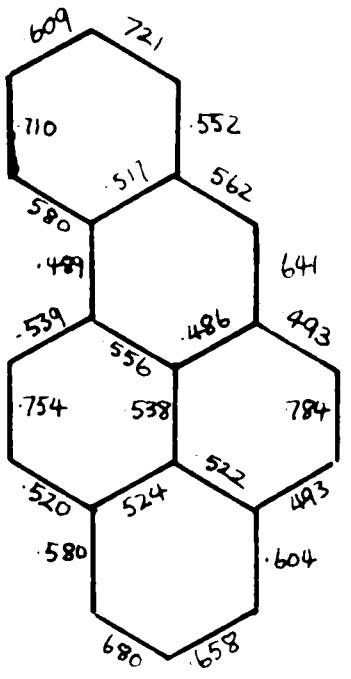
2.3 HMO calculations on some other pyrene benzologues

Clar (1963) recorded spectra of many molecules derived from pyrene by annelation in other directions as well as the mPn moleculesso far considered. These molecules may be given numerical names as follows:-

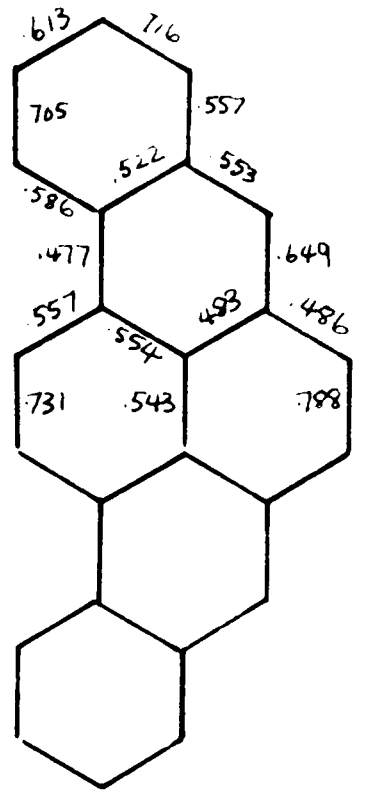
(a) Label the possible annelation axes with letters of the alphabet.

(b) Construct a symbol $\alpha m.P.\beta n$ where α, β are any of these letters and m, n are integers showing how many rings are linearly annelated in these directions.

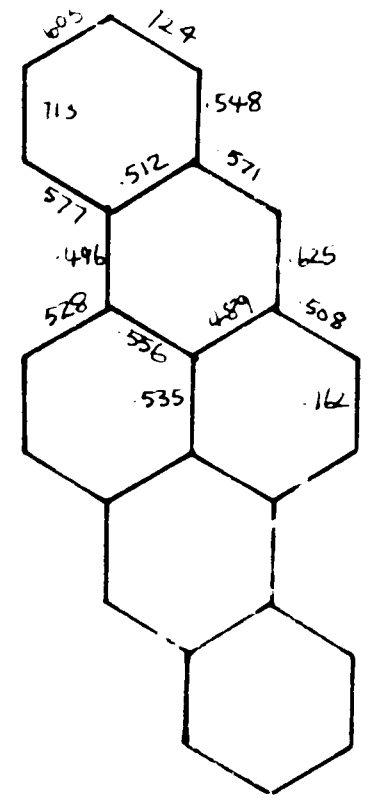
a1.P.o



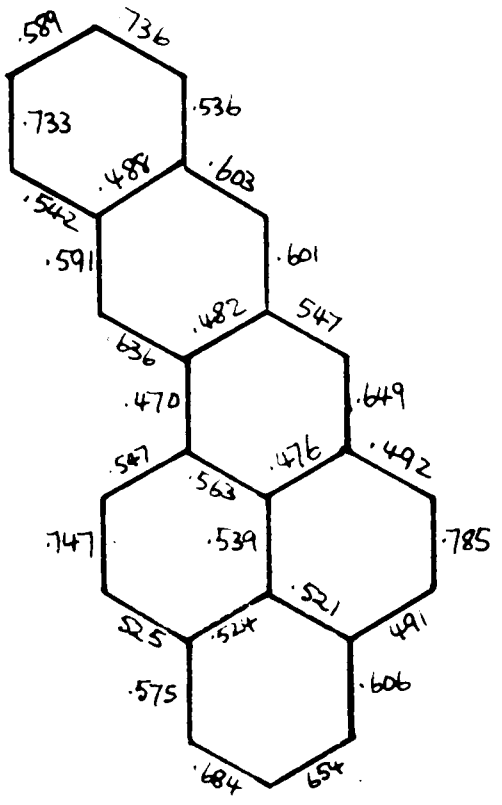
a1.P.cl



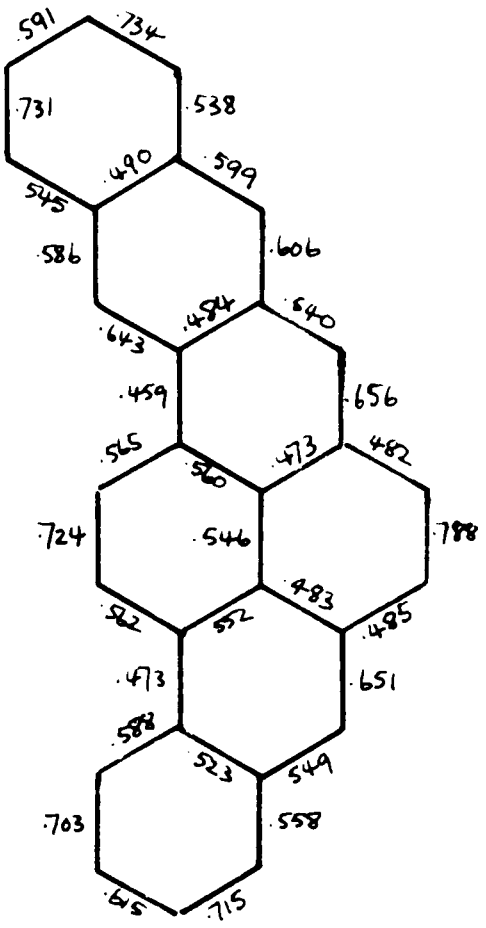
a1.P.d1



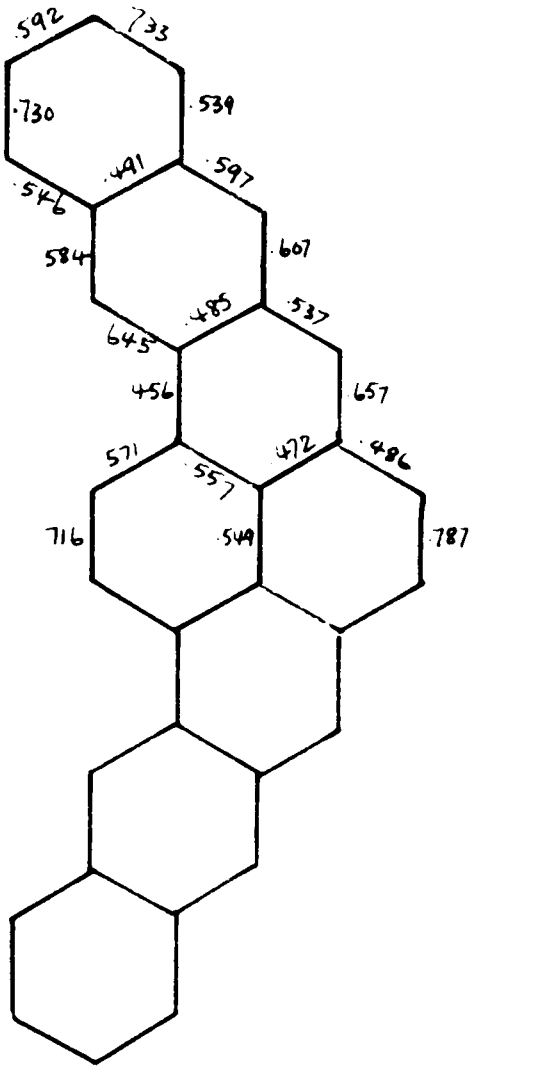
a2.P.o



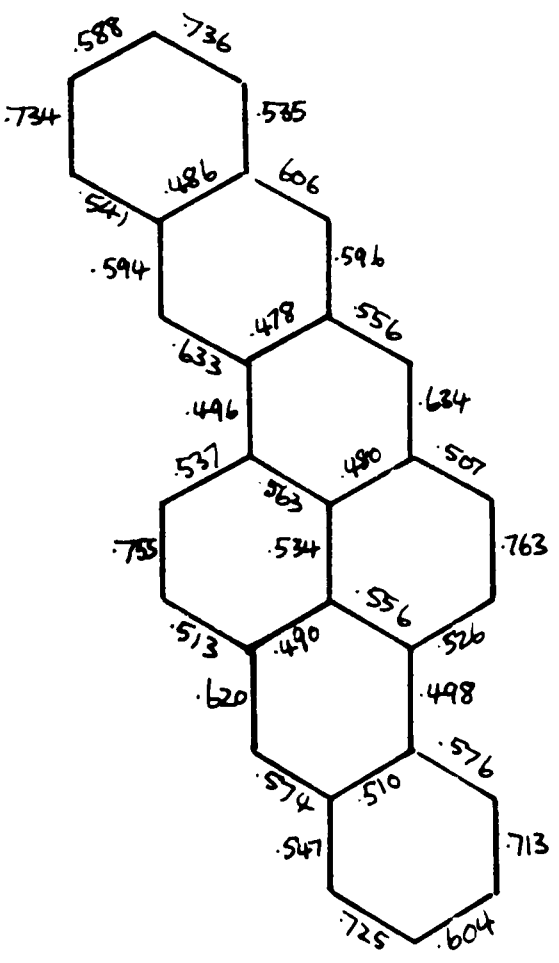
a2.P.cl



a2.P.d2



a2.P.d1



a2.P.d2

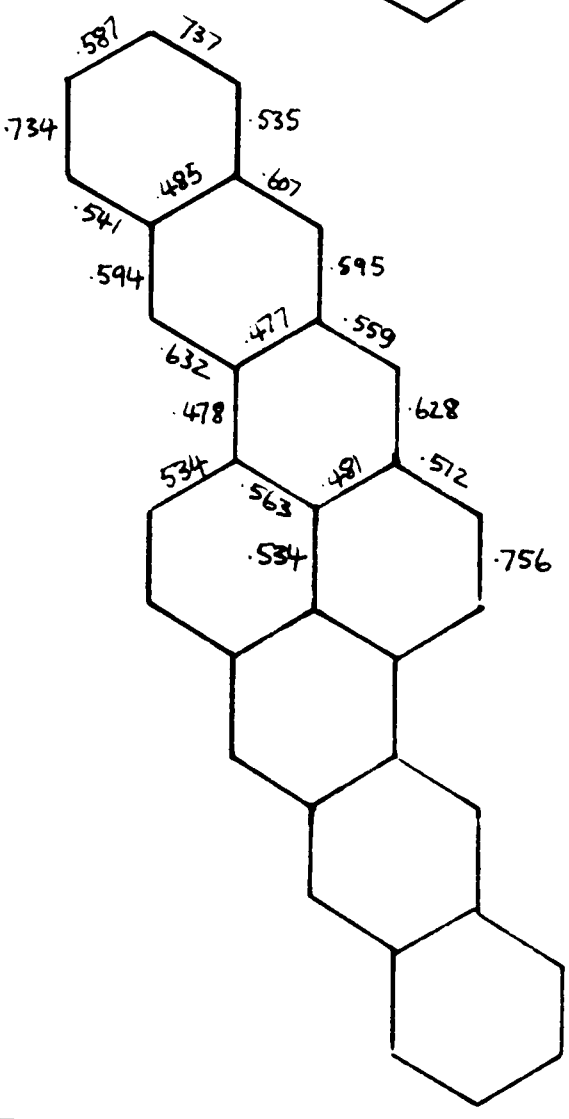
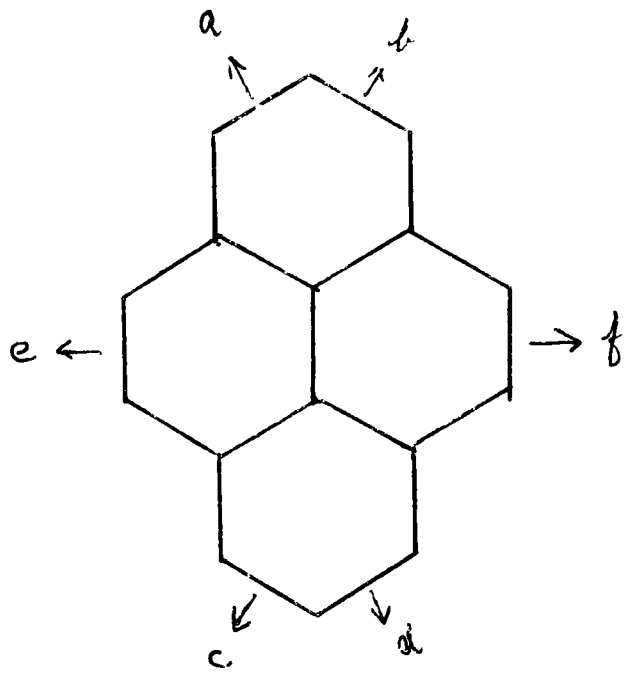


Fig 2.3 BOND ORDERS



The molecule 1.2-benz-pyrene may be called a1.P.O by this system, etc. Clar observed that the spectra of molecules annelated along the a and c, and a and d, pairs of axes showed the normal red shifts with further annelation. No asymmetric annelation effect was observed.

Hückel calculations have been carried out for these molecules and the bond orders calculated are represented in fig. 2.3. It should be noted that these molecules are not predicted to have any long bonds. The highest occupied orbitals, as might be expected, do not show any concentration at one end of the molecule and the energies show the expected changes on annelation. (The correlation of predicted energies and spectra is discussed further for all the molecules in Section 6.)

3. <u>The Longuet-Higgins - Murrell method</u>

Notation: L the 'left hand' fragment

R the 'right hand' fragment(s)

ϕ atomic orbitals

ψ molecular orbitals

Ψ_0 ground state determinantal wave function

$\psi_a^{-1}\,\psi_b$ or ab^* determinantal wave function for configuration with one electron excited from ψ_a to ψ_b

$(ab|cd)$ $\int \psi_a(i)\ \psi_b(i)\ \psi_c(j)\ \psi_d(j)\ \frac{1}{r_{ij}}\ d\tau_{ij}$

γ_{rt} $\int (\phi_r(i))^2\ \frac{1}{r_{ij}}\ (\phi_t(j))^2\ d\tau_{ij}$

r a suffix which ranges through atoms of L (usually)

t a suffix which ranges through atoms of R (usually)

$\sum_r^{\uparrow}(\sum_r^{\downarrow})$ for molecules with C_{2v} symmetry: Summation over all atoms r above (below) the symmetry axis.

$\sum_r^{L},(\sum_r^{\lrcorner},\sum_r^{\urcorner},\sum_r^{\Gamma})$ for molecules with D_{2h} symmetry: Summation over all atoms r in the 1st (2nd, 3rd, 4th) quadrant.

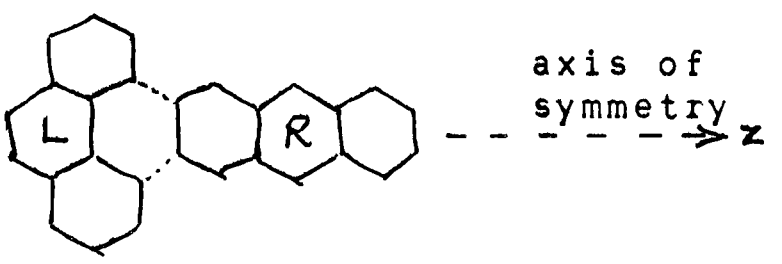
The first part of the analysis to be developed below is applicable to all molecules formed by joining fragments, later we shall particularize to those special cases for which programmes have been written, viz. the case of two benzenoid hydrocarbons with C_{2v} symmetry joined by a pair of bonds related by the axis of symmetry and the case of three benzenoid hydrocarbons the left and right fragments being identical and the middle fragment having D_{2h} symmetry; the four join bonds being such that the resulting molecule also has the full D_{2h} symmetry.

Examples are given below:

C_{2v} OP3

L = Phenanthrene

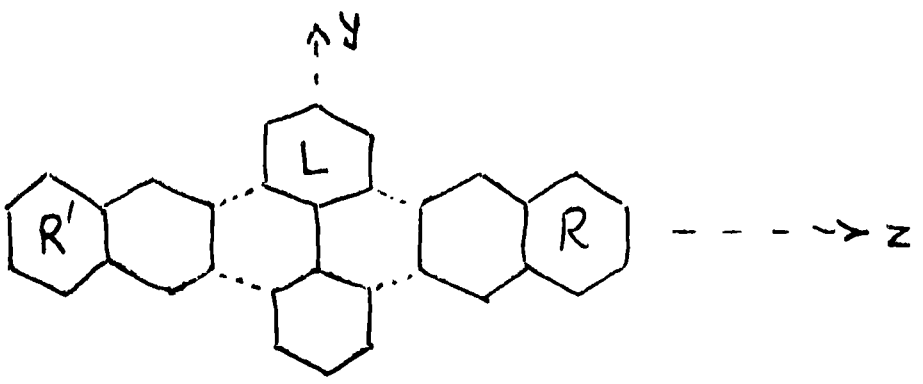
R = Anthracene



D_{2h} 2P2

L = Diphenyl

R = R' = Naphthalene



The extension to systems with 3 fragments without D_{2h} symmetry has not been carried out.

3.1 Configuration wave functions

Determinantal Wave functions for configurations are built up in the usual way (see e.g. Streitwieser (1961) Chapter 16) from the molecular orbitals of the fragments. The ground state wave function Ψ_o is thus given by:

$$\Psi_o = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1)\ \overline{\psi}_1(1) & \cdots\cdots\cdots & \psi_M(1)\ \overline{\psi}_M(1) \\ \psi_1(2)\ \overline{\psi}_1(2) & \cdots\cdots\cdots & \\ \vdots & & \\ \psi_1(N) & & \overline{\psi}_M(N) \end{vmatrix} \qquad (3.1)$$

written for short as $\frac{1}{\sqrt{N!}} |\psi_1(1) \ldots \overline{\psi}_M(N)|$

a bar indicates a β spin function, and there are a total of $N = 2M$ π-electrons (the σ-electrons are ignored completely except insofar as they contribute to the potential in which the π-electrons move).

Singly excited configurations.

If one electron is excited into a molecular orbital which is unoccupied in the ground state, a triplet or a singlet state arises according as the excited electron has the same spin or the opposite spin as the other in the vacated orbital. We shall concern ourselves here solely with the singlet states. As either an α or a β electron may be excited the correct wave function will be a sum of two determinants thus:

$$\psi_a^{-1}\ \psi_b = \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{N!}} \{ |\psi_1(1) \ldots\ \psi_a(i)\ \overline{\psi}_b(j) \ldots\ \overline{\psi}_M(N)| + |\psi_1(1) \ldots\ \psi_b(i)\ \overline{\psi}_a(j) \ldots\ \psi_M(N)| \} \qquad (3.2)$$

In order to carry out the configuration interaction calculation we must evaluate the matrix elements between functions of this sort for a suitable many-electron Hamiltonian operator. We use the operator used by Pople (1955):

$$\mathcal{H} = \sum_i H_i^{core} + \sum_{i<j} \frac{1}{r_{ij}} \qquad \text{(in atomic units)} \quad (33)$$

H^{core} represents the kinetic energy and the potential energy of the core of nuclei and σ-electrons.

General expressions for the matrix elements of $\mathcal{H}$ between configurational wave functions are given in the appendix to Pople's paper: (notation revised)

$$(\psi_a^{-1}\ \psi_b|\mathcal{H}|\ \Psi_0) = \sqrt{2}\ F_{ab} \qquad (3.4)$$

$$(\psi_a^{-1}\ \psi_b|\mathcal{H}|\psi_a^{-1}\ \psi_c) = F_{bc} + 2(ab|ac) - (aa|bc) \qquad (3.5)$$

$$(\psi_b^{-1}\ \psi_d|\mathcal{H}|\psi_c^{-1}\ \psi_d) = -F_{bc} + 2(bd|cd)-(bc|dd) \qquad (3.6)$$

$$(\psi_a^{-1}\ \psi_b|\mathcal{H}|\psi_c^{-1}\ \psi_d) = 2(ab|cd)-(ac|bd) \qquad (3.7)$$

$$\text{where } F_{ab} = (H^{core})_{ab} + \sum_{c=1}^{M} \{2(cc|ab)-(ca|bc)\} \qquad (3.8)$$

In order to simplify these matrix elements we expand the molecular orbitals in terms of atomic orbitals and neglect all terms involving the differential overlap ($\phi_r(i)\ \phi_s(i)$, $r \neq s$, under an integral sign).

$$\text{e.g. } (ab|cd) = \int \sum_r C_{ar}\ \phi_r(i) \sum_s C_{bs}\ \phi_s(i) \sum_t C_{ct}\ \phi_t(j) \sum_u C_{du}\ \phi_u(j)\ \frac{1}{r_{ij}}\ d\tau_{ij} \qquad (3.9)$$

Because of neglect of differential overlap, unless <u>both</u> r and s range over the same set of atoms <u>and</u> t and u range over the same set of atoms, this integral will vanish.

If this integral occurred in the above formulae with a factor 2, this means that only a pair of locally excited configurations will give a non-zero term. If, on the other hand, it occurred as the final term with a factor -1 only

a pair of locally excited configurations of the same fragment, or of charge-transfer configurations representing transfer in the same direction will give a non-zero term. In these circumstances it simplifies to:

$$(ab|cd) = \sum_r \sum_t C_{ar}\, C_{br}\, C_{ct}\, C_{dt}\, \gamma_{rt} \qquad (3.10)$$

If a and b are orbitals of different fragments we get from the definition of F_{ab}, the second term going out:

$$F_{ab} = (H^{core})_{ab} = \int \psi_a(i)\, H_i^{core}\, \psi_b(i)\, d\tau_i$$

$$= \int \sum_r C_{ar}\, \phi_r(i)\, H_i^{core} \sum_t C_{bt}\, \phi_t(i)\, d\tau_i$$

$$= \sum_{\substack{\text{all bonds } r\text{-}t \\ \text{between fragments}}} C_{ar}\, C_{bt}\, \beta_{rt}, \qquad (3.11)$$

where we neglect all matrix elements of H_i^{core} between atomic orbitals except those which are bonded. For these we let the matrix element be β_{rt}.

Since by definition SCF orbitals diagonalize the F-matrix we may reasonably neglect all off-diagonal elements F_{ab} when a, b are orbitals of the same fragment, if our molecular orbitals are approximately self-consistent. For alternant hydrocarbons this is known to be true for Hückel orbitals, so for the sake of simplicity we shall use these.

We have now considered all possible types of matrix element except the diagonal elements. Taking the energy of the ground state as zero we use the experimentally observed transition energy for the diagonal elements of locally excited states; in this way we introduce a semi-empirical side to the method which might be expected to make up in part for the crudity of some of the other approximations made. For the charge transfer states we combine experiment and calculation: The energy of the state is approximately equal to the ionization potential of the donor fragment,

less the electron affinity of the acceptor fragment, less the electrostatic interaction calculated from an equation like (3.10).

If in an obvious notation we call the possible γ-terms γ_2 and γ_{-1} and call the F terms β and those derived from experiment Ex the following table summarizes the types of matrix element possible.

	Local left	Charge transfers		Local right
	0 LL*	1 LR*	2 RL*	3 RR*
0 L'L*'	0 Diag: Ex Non Diag: $\gamma_2+\gamma_{-1}$	1 L=L': β L≠L': 0	2 L*=L*': β L*≠L*': 0	3 γ_2
1 L'R*'	4=1	5 Diag: Ex+γ_{-1} Non Diag: γ_{-1}	6 0	7 R*=R*': β R*≠R*': 0
2 R'L*'	8=2	9=6	10 Diag: Ex+γ_{-1} Non Diag: γ_{-1}	11 R=R': β R≠R': 0
3 R'R*'	12=3	13=7	14=11	15 Diag: Ex Non Diag: $\gamma_2+\gamma_{-1}$

The discussion of what values should be used for the experimental quantities is left until later; we now consider the calculation of the β and γ terms and the subsequent solution of the configuration interaction problem.

3.2 Calculations

The only parts which involve non-trivial calculation are the calculation of the γ matrix elements and the diagonalization of the configuration interaction matrix. However, if one is going to use the computer at all one might as well do the whole calculation on the computer and so the whole problem was programmed for Mercury.

As the calculations involve large numbers of integers, (atom numbers, orbital numbers, configuration numbers, coordinates of atoms in a plane hexagonal lattice, etc.) and great simplifications of the calculation may be made by using symmetries of orbitals, the properties of alternant hydrocarbons and their molecular orbitals, which are most simply dealt with by using logical variables (binary numbers considered as bit-patterns rather than integers) the problem was treated as an exercise in machine-language programming and certain features of the order code were found especially useful.

Because of the advantages of being able to use the standard Autocode compiler, its built in subroutines and the library Programme - 517 for diagonalizing the matrix, the programme, although mostly in machine language form was written in the Autocode framework and Autocode instructions were used where these do not reduce the efficiency of the object programme.

Two versions have been written which will be described as the C_{2v} version and D_{2h} version respectively.

The C_{2v} version may be used for any benzenoid hydrocarbon (necessarily alternant) which has C_{2v} symmetry

and is to be considered built up from two fragments L and R by a single pair of join bonds related by the symmetry axis.

The D_{2h} version may be used for any benzenoid hydrocarbon with D_{2h} symmetry which is considered to be built up from three fragments R', L and R by a set of 4 join bonds related by the axes of symmetry.

The data for the calculation consists of (1) a description of the geometry of the two fragments; (2) The relevant molecular orbitals of the fragments; (3) the configurations to be considered and (4) information as to where the molecules are to be joined and the value of β to be assumed for the join bonds. Since all carbon $2p\pi$ orbitals are assumed the same the values of the electron interaction integrals γ_{rt} are a function solely of the distance apart of atoms r and t. Various formulae for γ_{rt} as a function of R_{rt} have been proposed (see e.g. **Pariser** and Parr 1953). Because of the crudity of the present calculations we have chosen the approximation used by **Pariser** and Parr for short distances:

$$\gamma_{rt} = 0.2157\ R_{rt}^2 - 2.625\ R_{rt} + 10.53 \text{ eV} \quad (R \text{ in } \mathring{A}) \quad (3.12)$$

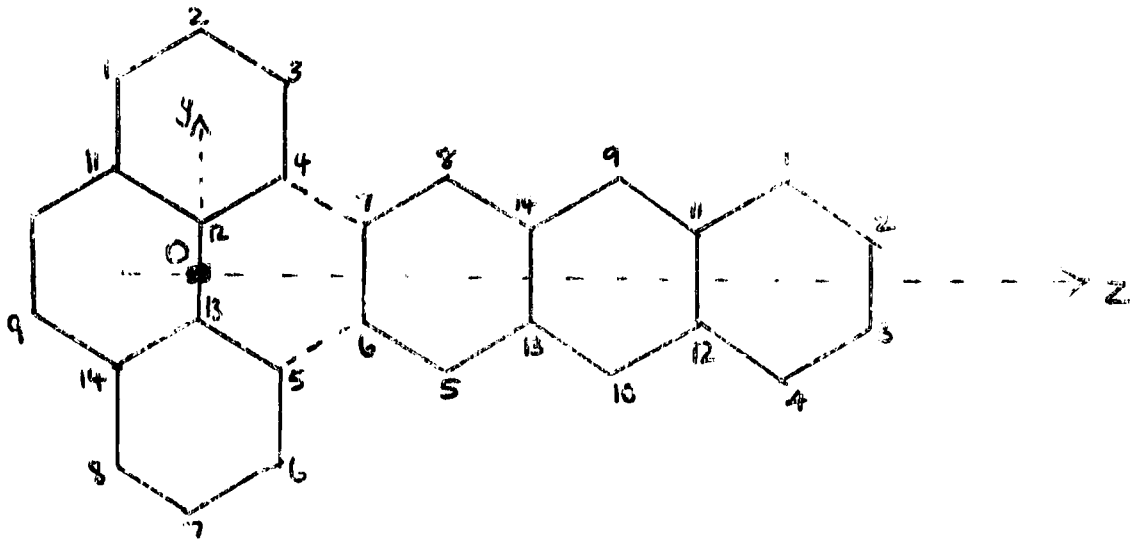
for longer distances it is adequate to assume γ inversely proportional to the distance and take

$$\gamma_{rt} = \frac{14.42}{R_{rt}} \text{ eV} \quad (3.13)$$

These formulae give the same γ for $R \approx 5.52\ \mathring{A}$ and so this is used as the value for changing from (3.12) to (3.13).

3.21 <u>The form of the data</u> (1) The geometry.

As an example let us consider the molecule OP3



To describe the geometry of the fragments we need merely to list the z- and y-coordinates of the atoms. We take an origin on Oz arbitrarily at the middle of the 12-13 bond of phenanthrene and use as units $\frac{\sqrt{3}}{2}\, r_{C-C}$ in the z-direction and $\frac{1}{2} r_{CC}$ in the y-direction (r_{CC} is taken to have the standard benzene value 1.39Å). These two integer coordinates may be stored in two of the four 10-bit half registers which make up a Mercury <u>word</u>. So that the later data may refer to atoms by their numbers the other two half-registers are filled with the numbers of the atoms above and below the axis. In order to divide the alternant molecule into starred and non-starred sets, all pairs of atoms, the y-coordinate of the atom above Oz of which $\equiv 2$ (modulo 3), have 512 added to their second atom numbers. The sign digit of this half-register is then a Boolean variable with value 1 for a starred atom (say) and 0 for a non-starred. (Strictly speaking a <u>Boolean</u> variable has one of the values <u>true</u> or <u>false</u>, here the digit 1 is the <u>computer representation</u> of the value **true** the variable being the statement: "Atom r is starred".)

The form of this part of the data for the L fragment

of OP3 after modification by the programme is thus:

1	8	-1	4
2	-505	0	5
3	0	1	4
4	-507	1	2
10	9	-2	1
11	-498	-1	2
12	13	0	1

(2). The orbitals

The aim in this part has been to keep the amount of data to an absolute minimum; to save time in preparation and input and to save storage space in the machine. Since the fragments are alternant the 'complementary' property may be used to derive MO coefficients for anti-bonding orbitals from the stored coefficients for bonding orbitals. The presence of a symmetry axis means that coefficients need be given only for atoms above this axis, provided also that the symmetry of the orbital is given. As the orbitals may well have been calculated by the HMO programmes of Chapter I, this part of the data is made acceptable when in the form in which the orbitals are tabulated by the HMO programmes. The orbitals are thus to be tabulated in blocks, each block to be preceded by the number of orbitals it contains (+ 100 for all blocks except the first one for each fragment). Each block consists of a row of orbital numbers, a row of symmetry labels, and rows of MO coefficients, which may be preceded by the corresponding atom numbers if desired. Atom numbers, being necessarily ≥ 1 are easily distinguished from coefficients

which are < 1 and so are ignored by the programme. The one condition on this part of the data is that the rows representing the coefficients of the atomic orbitals shall appear in the same order as the corresponding sets of atom numbers and coordinates in the 'geometry'.

For each orbital read in a codeword is constructed. A set of four 10-bit registers making up a word is used for this. The first part is a Boolean variable representing the truth value of "this orbital is antisymmetric about Oz", the second is the orbital no. (which has 512 added to it if it is an orbital of R), the third is not used and the fourth is the address of the first coefficient of this orbital. This codeword is used solely for constructing configuration codewords.

Complementary orbitals have a codeword but no separate storage of coefficients. To ensure that appropriate codewords are generated the occupied orbitals must be followed by a single integer whose value is minus the number of complementary orbitals wanted. The first complementary orbital will be given the next orbital number after the highest so far read in, that complementary to the top but one the next, and so on.

(3) The configurations

Each configuration is represented by four quantities: the <u>type</u>, the <u>vacated</u> orbital number, the <u>acceptor</u> orbital number and the experimental part of the diagonal matrix element (in eV). The type is one of: L $\longrightarrow$ L, L $\longrightarrow$ R, R $\longrightarrow$ L or R $\longrightarrow$ R describing whether the configuration is locally excited or electron transfer and to which

fragment the relevant orbitals belong. The type L ⟶ R is thus an electron transfer configuration involving excitation of an electron from an orbital of L to one of R. The configuration codeword starts with a representation of the type which consists of binary digits in the 2^1 and 2^0 positions whose value is 0 for L and 1 for R. (e.g. L ⟶ R is represented by 01). These numbers are shown on the table of matrix element types on p. 105 above. The vacated and acceptor orbital numbers are converted on input (by searching the orbital codewords) to the corresponding addresses of the first orbital coefficients. These go into parts 2 and 3 of the codeword. The fourth part is another 2-digit number the first representing the symmetry of the vacated orbital, the second that of the acceptor orbital.

The list of configurations is preceded by an integer - the number of configurations listed.

(4) The join data

This consists of three numbers: the value of β (in eV) to be used for the join bonds, and the atom numbers of the atoms of L, R respectively which are joined by the join bond on the positive side of Oz. These atom numbers (converted into ordinal numbers in the list of atom sets) form a 2-part join codeword.

The form of a complete data tape

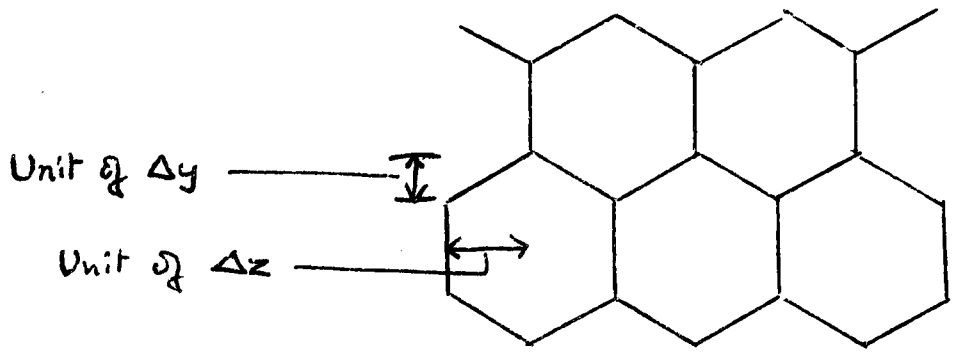
A complete data tape starts with a heading which (as for the HMO programmes) is any sequence of characters terminated by 'n' or '?'. Then part (1) for L, part (1) for R, part (2) for L, part (2) for R, part (3) and part (4). If further calculations on the same molecule but

with different configurations and/or value of β for the join are required, a shortened form of data tape consisting of a heading and parts (3) and (4) may be used which is read in with handswitch 5 up and causes the other data to be used again.

3.22 The calculation of the matrix elements and the solution of the configuration interaction problem

3.221 The matrix of γ_{rt}'s

As the same value of γ_{rt} will arise for several different pairs of r, t and the programme was designed to be adaptable to use any formula for γ_{rt} as a function of R_{rt}, a matrix of values of γ_{rt} is calculated once and for all and values are extracted by specifying Δz and Δy (in units of $\frac{\sqrt{3}}{2}\, r_{C-C}$ and $\frac{1}{2} r_{C-C}$ respectively) for the particular r, t being considered.



A glance at the figure will show that only those values of Δz, Δy need be considered for which $\Delta z + \Delta y$ is even.

To keep this matrix to a minimum size the minimum and maximum z- and y-coordinates are noted when reading in the geometry and a codeword [I, J, K, L] is constructed as follows:

[Max Δy, - , Max Δz (-1 if Max Δy is odd), Number of Δz's tabulated for each Δy]

A rectangular matrix is then constructed so as to include all possible pairs of Δy, Δz consistent with the maxima

determined. These are stored in the order: (each pair represents (Δy, Δz)). (0, 0) (0, 2) (0, 4) ... (0, K) (1, 1) (1, 3) ... (1, K+1) (2, 0) (2, 2) .... (I, K).

The value of K and a pair of integers Δy, Δz are thus required to specify an element of this matrix.

3.222 The symmetries of configurations

It is possible by studying the behaviour of configurational wave functions under the operations of the symmetry group to determine to which irreducible representation each configuration belongs. This, however, is not necessary in the present case as configurations may be split simply into those which are symmetric and those which are anti-symmetric with respect to relfection in the one (C_{2v}) or 2 (D_{2h}) planes of symmetry at right angles to the molecular plane. The 'multiplication table' for the symbols S and A is seen to be isomorphic to the table for the logical operation of non-equivalence on the binary digits 0 and 1 respectively.

X	S	A
S	S	A
A	A	S

≠	0	1
0	0	1
1	1	0

This operation, which is available in the Mercury machine code, may thus be used to combine symmetries when these are represented as in the orbital codeword described above. It should further be noted that when there are two planes of symmetry adjacent digits of a 10-bit number may be used to represent symmetry with respect to these planes and the operation of non-equivalence will operate on them separately. This method of representing symmetry will be

adequate for all cases where all representations of the group are one-dimensional.

By using this property the configurations may easily be split into the different symmetry species as they are read in. The upper triangle of the interaction matrix is then set up element by element for each symmetry. From the two configuration types the appropriate matrix element subroutine is chosen by multiplying one type by 4 and adding the other, thus giving the position in the table on p. 105 The sixteen different positions on the table are correlated with the six types of matrix element (represented by a code character punched on the output tape) as follows:†

	LL*	LR*	RL*	RR*
LL*	0	1	2	3
LR*	4	5	6	7
RL*	8	9	10	11
RR*	12	13	14	15

Matrix element type

0	1	2	3
1	5	6	2
2	6	5	1
3	2	1	0

code character

8	7	)	(
4	*	2	1
1	2	*	4
(	)	7	8

The subroutines in the programme are given entry labels equal to the matrix element type +120.

3.223 Matrix elements of types 1; 2 (code characters 7, 4;), 1). These are the β-type matrix elements, which are non-zero when the configurations are (1): a local excitation and an electron transfer from the same vacated orbital, or (2): a local excitation and an electron transfer to the same acceptor orbital. Only the first terms of the right hand sides of equations (3.5) and (3.6) survive (for the reasons given below equation (3.9)) and, using (3.11) they become:

† The 'code character' is that character in the tape code whose binary representation is 8-p for p≤7 and p-7 for p≥8 where p is the position in the left-hand table. The pairs of characters 7 and 4,) and ! correspond to subroutines for matrix elements of types 1,2 respectively. Other correspondences are 1↔1. Note that the names L, R are interchangeable.

type 1: $(\psi_a^{-1}\ \psi_b|\mathcal{H}|\psi_a^{-1}\ \psi_c) = \sum_{\substack{\text{join bonds}\\ r-t}} C_{br}\, C_{ct}\, \beta_{rt}$ (3.14)

type 2: $(\psi_b^{-1}\ \psi_d|\mathcal{H}|\psi_c^{-1}\ \psi_d) = -\sum_{\substack{\text{join bonds}\\ r-t}} C_{br}\, C_{ct}\, \beta_{rt}$ (3.15)

Both these terms go out unless the two orbitals involved have the same symmetry. In type 1 both b, c will be antibonding orbitals and hence stored as complementary orbitals. Since one only of the atoms r, t must belong to the starred set the product $C_{br}\, C_{ct}$ must equal $-C'_{br}\, C'_{ct}$, the primed coefficients being the ones stored. If S_a is the computer representation of the symmetry of a we have:

types 1 and 2

$$(\psi_a^{-1}\ \psi_b|\mathcal{H}|\psi_a^{-1}\ \psi_c) = -c'_{br}\, c'_{ct}\, \beta(1 + (-1)^{S_b \neq S_c})$$

$$= (\psi_b^{-1}\ \psi_d|\mathcal{H}|\psi_c^{-1}\ \psi_d) \qquad (3.16)$$

These types may thus be calculated by effectively the same subroutine.

3.224 Matrix elements of types O, 3, 5 (code characters: 8, (,*)

These are the γ-matrix elements and we will first show how the expression for a general type O element is adapted to take full advantage of the symmetry and complementarity properties of the orbitals.

$$(\psi_a^{-1}\ \psi_b|\mathcal{H}|\psi_c^{-1}\ \psi_d) = 2(ab|cd) - (ac|bd)$$

$$= 2\sum_{r,t} c_{ar}\, c_{br}\, c_{ct}\, c_{dt}\, \gamma_{rt}$$

$$- \sum_{r,t} c_{ar}\, c_{cr}\, c_{bt}\, c_{dt}\, \gamma_{rt}$$

$$= \sum_r^{\uparrow} \sum_t^{\uparrow} (2c_{ar}\, c_{br}\, c_{ct}\, c_{dt}\{\gamma_{rt}^{\uparrow\uparrow} + (-1)^{Sa \neq Sb}\, \gamma_{rt}^{\downarrow\uparrow} + (-1)^{Sc \neq Sd}\, \gamma_{rt}^{\uparrow\downarrow} + (-1)^{Sa \neq Sb \neq Sc \neq Sd}\, \gamma_{rt}^{\downarrow\downarrow}\}$$

$$- c_{ar}\, c_{cr}\, c_{bt}\, c_{dt}\{\gamma_{rt}^{\uparrow\uparrow} + (-1)^{Sa \not\equiv Sc}\, \gamma_{rt}^{\downarrow\uparrow} + (-1)^{Sb \not\equiv Sd}\, \gamma_{rt}^{\uparrow\downarrow} + (-1)^{Sa \not\equiv Sb \not\equiv Sc \not\equiv Sd}\, \gamma_{rt}^{\downarrow\downarrow}\}) \quad (3.17)$$

$\gamma_{rt}^{\uparrow\uparrow}$ is the γ integral between the atom of set r of L above the axis and the atom of set t of R above the axis, etc.

Now $Sa \not\equiv Sb = Sc \not\equiv Sd$ = symmetry of configurations $\psi_a^{-1}\, \psi_b$, $\psi_c^{-1}\, \psi_d = P$ (say). Similarly $Sa \not\equiv Sc = Sb \not\equiv Sd = Q$(say); also $Sa \not\equiv Sb \not\equiv Sc \not\equiv Sd \not\equiv O$. so we have:

$$2(ab|cd)-(ac|bd) = 2 \sum_r^{\uparrow} \sum_t^{\uparrow} (2c_{ar}\, c_{br}\, c_{cr}\, c_{dt}\{\gamma_{rt}^{\uparrow\uparrow} + (-1)^P \gamma_{rt}^{\uparrow\downarrow}\} - c_{ar}\, c_{ct}\, c_{bt}\, c_{dt}\{\gamma_{rt}^{\uparrow\uparrow} + (-1)^Q\, \gamma_{rt}^{\uparrow\downarrow}\}) \quad (3.18)$$

orbitals b and d are acceptor, and hence antibonding, orbitals which are stored as their complements. Using primed c's to indicate the coefficients actually stored this gives the final formula

$$2(ab|cd)-(ac|bd) = 2 \sum_r^{\uparrow} c'_{ar} \{\sum_t^{\uparrow} c'_{dt}[2c'_{br}\, c'_{ct}(\gamma_{rt}^{\uparrow\uparrow} + (-1)^P \gamma_{rt}^{\uparrow\downarrow})^{(-1)^{A_r \not\equiv A_t}} - c'_{cr}\, c'_{bt}(\gamma_{rt}^{\uparrow\uparrow} + (-1)^Q\, \gamma_{rt}^{\uparrow\downarrow})]\} \quad (3.19)$$

The quantity $A_r \not\equiv A_t = 1$ when atoms r, t are in different sets.

The quantity $A_r \not\equiv A_t = O$ when atoms r, t are both starred, or both unstarred.

This formula is used to compute off-diagonal matrix elements of type O, diagonal ones being taken from experiment. Matrix elements of type 3 are calculated from the first term γ_2 of (3.19) only. Elements of type 5 from the second term γ_{-1} with experimental data added if the element is on the diagonal of the configuration

interaction matrix.

Elements of type 6 are zero.

When the matrix has been set up its eigenvalues are found by the Autocode library programme -517 and printed out. The eigenvector for the lowest state is also printed so that one may see which configurations are chiefly represented therein.

For the C_{2v} molecules this is carried out first for the antisymmetric configurations which are those to which transition from the ground state are allowed. If there are also symmetric configurations low enough to interact with the ground state these are also treated. The matrix elements between the ground state and electron transfer states being calculated using (3.4).

3.23 Differences in the Programme for D_{2h} molecules

3.231 The data

The content of the data is the same as for the C_{2v} molecules, the origin of coordinates being necessarily fixed at the centre of symmetry. A slight change in order was made for greater convenience of preparation of data tapes: this is that the geometry and orbitals of L precede the geometry and orbitals of R instead of being 'interleaved.' Since R now consists of two fragments R and R' correct linear combinations of orbitals of both must be made to conform with the overall D_{2h} symmetry. All this is done entirely by the programme and the user need not bother about which configurations have the correct symmetry. In fact any mention of an orbital ψ_a of R in the list of configurations is interpreted as referring to the orbital

$\frac{1}{\sqrt{2}}(\psi_a + \psi'_a)$ where ψ'_a is an orbital of R' followed by an equivalent reference to $\frac{1}{\sqrt{2}}(\psi_a - \psi'_a)$. Configurations of type L ⟶ R and R ⟶ L are thus really pairs of configurations with opposite symmetry about Oy and configurations of type R ⟶ R are sets of four configurations, two symmetric and two antisymmetric about Oy.

3.232 Evaluation of matrix elements

β-type matrix elements: the formula corresponding to (3.16) is:

$$(\psi_a^{-1}\psi_b|\mathcal{H}|\psi_a^{-1}\psi_c) = -C'_{br}\,C'_{ct}\beta(1+(-1)^{S_{bz}\neq S_{cz}})(1+(-1)^{S_{by}\neq S_{cy}}) \quad (3.20)$$

γ-type matrix elements: the formula corresponding to (3.19) is:

$$4\sum_r^L c'_{ar}\{\sum_t^{\uparrow} c'_{dt}[2c'_{br}c'_{ct}(\gamma_{rt}^{LL}+(-1)^{Pz}\gamma_{rt}^{L\Gamma}+(-1)^{Py}\{\gamma_{rt}^{LJ}+(-1)^{Pz}\gamma_{rt}^{L\urcorner}\}).(-1)^{A_r\neq A_t} - c'_{cr}\,c'_{bt}(\gamma_{rt}^{LL}+(-1)^{Qz}\gamma_{rt}^{L\Gamma}+(-1)^{Qy}\{\gamma_{rt}^{LJ}+(-1)^{Qz}\gamma_{rt}^{L\urcorner}\})]\} \quad (3.21)$$

3.3 The programmes

Flow charts for the C_{2v} and D_{2h} versions of the programme are given as charts III.1-III.4. An annotated print-out of the D_{2h} programme is given as Appendix A to this Chapter. The C_{2v} version is not sufficiently different to warrant separate inclusion and so is omitted.

3.31 Size limitations

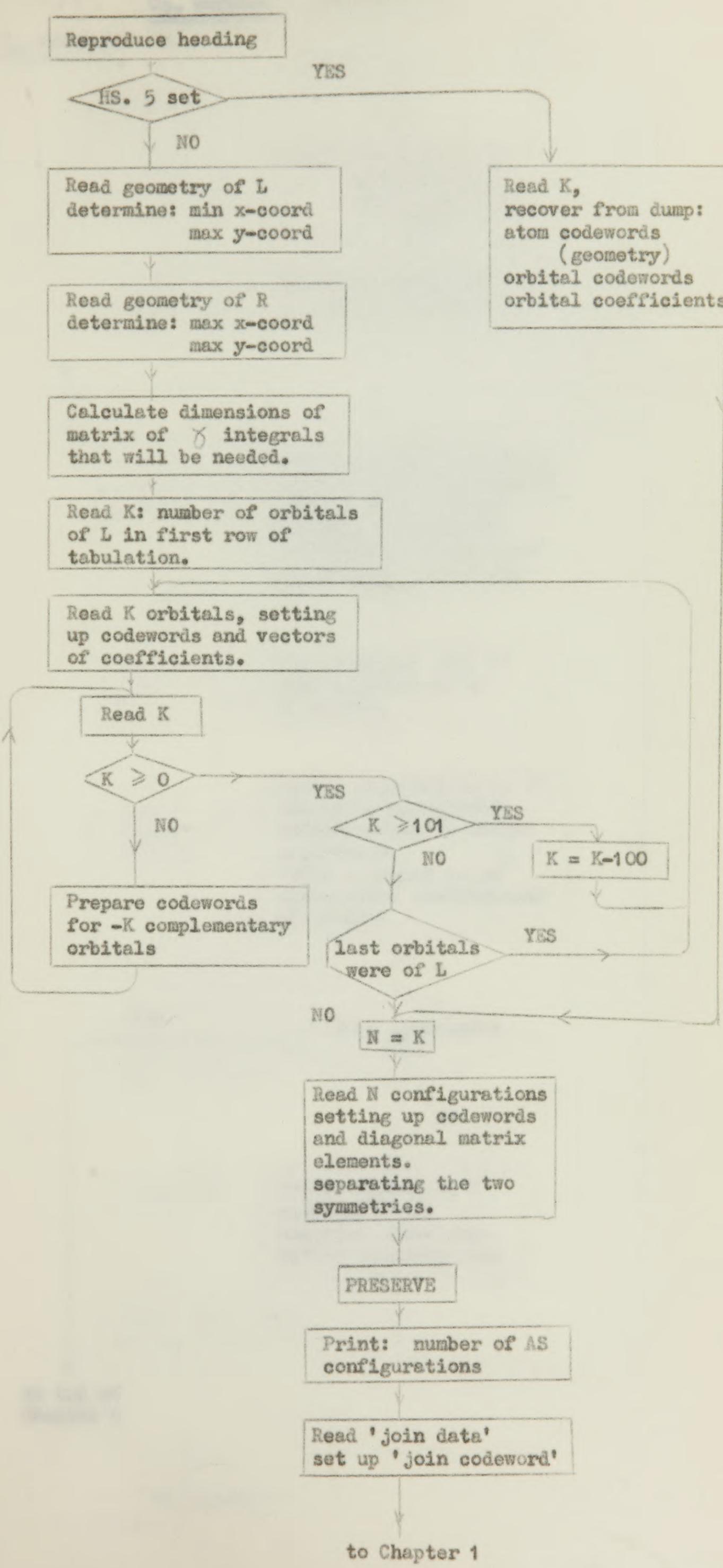
In order to reduce the number of auxiliary transfers to a minimum the following limitations on the sizes of molecules and numbers of configurations that may be considered are imposed.

	Quantity	Maximum	
		C_{2v}	D_{2h}
1.	sets of atoms related by symmetry in L	32	16
2.	sets of atoms related by symmetry in R	32	32
3.	max $\Delta y[1+\frac{1}{2}(\max \Delta x)]$	176	164
4.	MO coefficients	144	124
5.	orbitals (including implied complementary)	32	24
6.	configurations - any one symmetry	16	12
7.	configurations - total	32	32

The restriction which is likely to be met first in practice is no. 3. The reason for this restriction is that a great saving of time is made if all possible γ_{rt} integrals for a given molecule can be calculated once for all and kept in the fast store of the computer. As the order in which these quantities are required when computing a formula such as (3.21) is not easily systematized it would have been difficult to design a simple system for having the γ_{rt} in the auxiliary store and reading in the ones wanted for each term of (3.21).

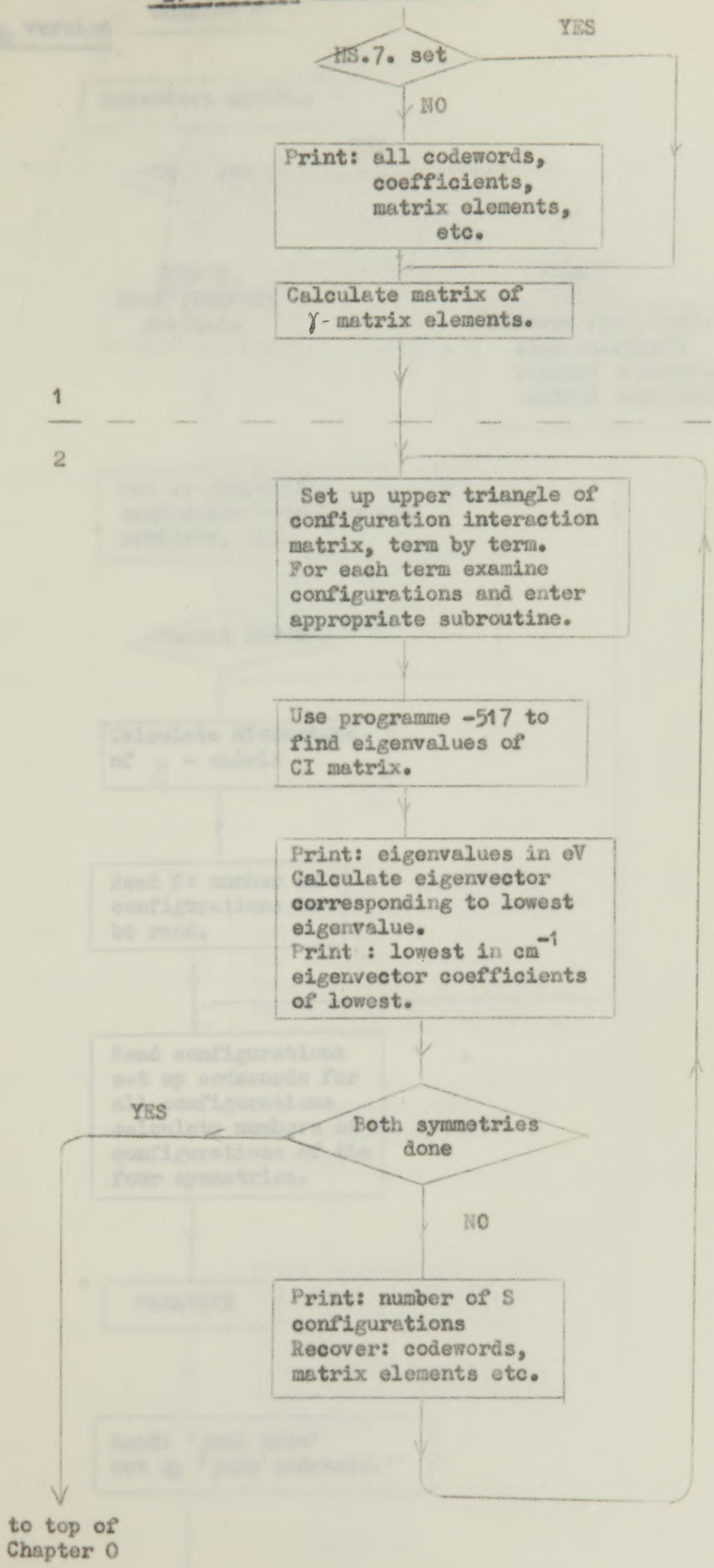
Restrictions 6 and 7 limit the number of configurations which may be considered for any molecule; however, the difficulty of choosing suitable diagonal matrix elements for these configurations makes the reliability of a calculation including many of them rather doubtful and it is considered that one should not expect to get very much better results than by merely taking the absolute minimum number of configurations.

C2v version
Chapter 0



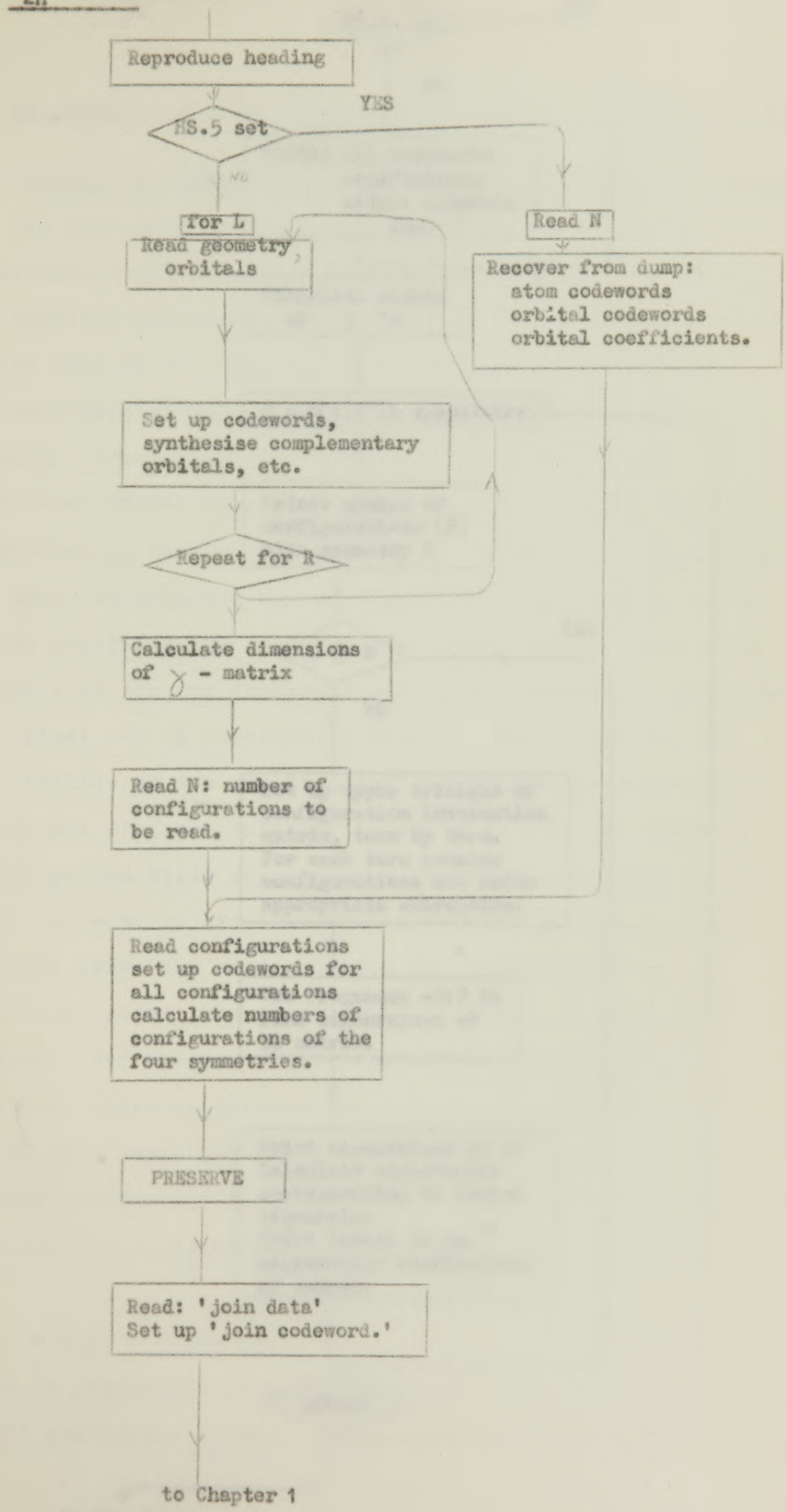
Flow chart III.2

C_{2v} version Chapters 1,2

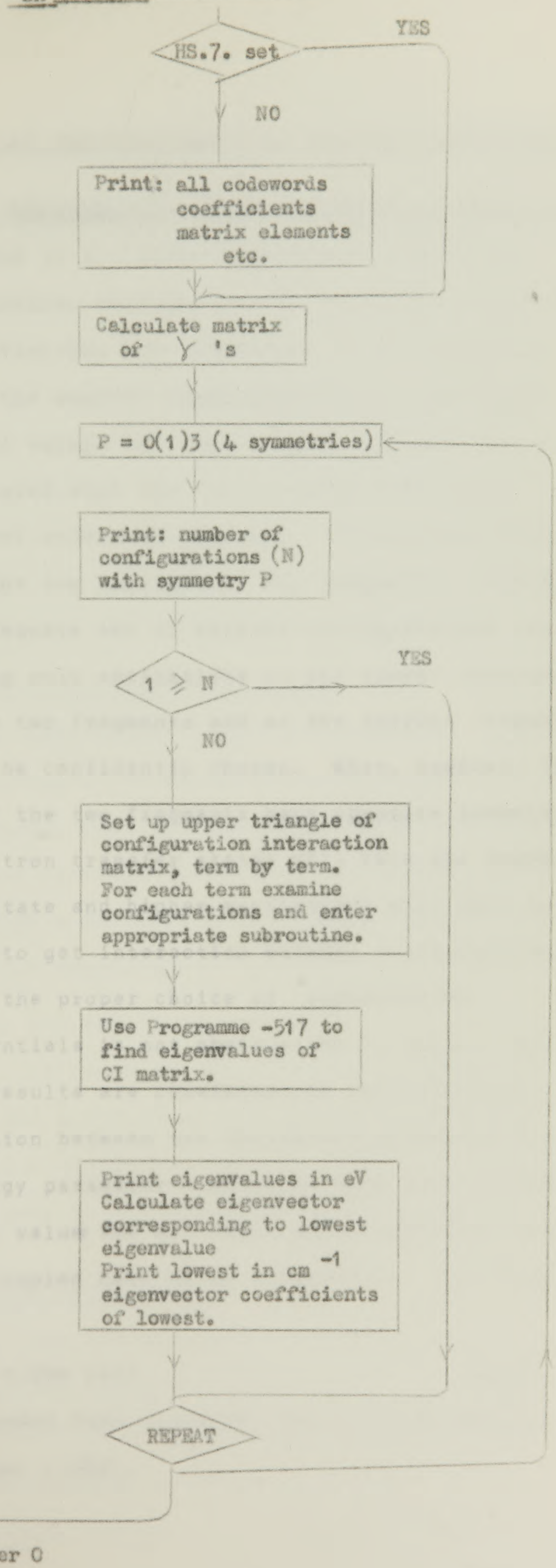


Flow chart III.3

D_{2h} version Chapter 0



D_{2h} version Chapters 1, 2



to Chapter 0

4. Application of the Programmes to the Benzologues of Pyrene

4.1 Choice of 'Experimental' data for diagonal matrix elements

As explained in 3.1 above experimental values of electronic transition energies and of ionization potentials and electron affinities are introduced in an attempt to make up for some of the drastic approximations in the method. The experimental values for these quantities may only be reliably correlated with the top occupied and lowest unoccupied Hückel molecular orbitals. Fortunately when the symmetries of the top orbitals of the fragments L and R are the same, an adequate set of excited configurations can be chosen involving only excitations to the lowest unoccupied orbitals in the two fragments and so the correct 'experimental' values can be confidently chosen. When, however, the top orbitals of the two fragments have opposite symmetries the lowest electron transfer states will have the symmetry of the ground state and higher excitations will have to be taken in order to get interaction between configurations. In these cases the proper choice of 'experimental' ionization potentials is not obvious and to ensure that, at least, our results are consistent, we have chosen an empirical relation between the ionization potential I and the Hückel energy parameter m which we have used instead of experimental values for all cases where orbitals other than the top occupied have to be considered. The formula is:

$$I = 5.51 + 4.04m \text{ (ev)} \qquad (3.22)$$

which is compounded from formulae due to Streitwieser (1961) and Matsen (1956).

Values of I and electronic transition energies were taken from the compilation of Matsen (1956).

Values of the electron affinities A were taken where possible from Hedges and Matsen. (1958). Where values for both fragments were not available they were taken to be zero. This seems a somewhat drastic assumption, but as those values which are known are doubtful because of the difficulty of allowing for solvation energy when they are determined in solution, and are small compared with the ionization potentials, it is not considered that the results will be seriously out as a result of this assumption.

4.2 The value of β for the join bonds

Pariser and Parr (1953) recommend using β = - 2.39 ev for standard Benzene C - C bonds in configuration interaction calculations. Coulson and Golębiewski (1961) suggest an expression for variation of β with bond length, which when combined with a suitable order-length relationship (see II.1 eqn. 1.4 above) gives the formula:

$$\beta(p) = \beta_o \exp\{-2.683\ (0.12 - 0.18p)\} \qquad (3.23)$$

using p = 0.420 (as found for all the join bonds by the Hückel method) and β_o = -2.39 we get for the join bonds:

$$\beta = -2.12 \text{ eV}. \qquad (3.24)$$

which has been used in all the present calculations.

5. Results of the calculations

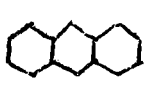
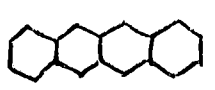
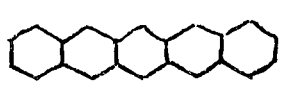
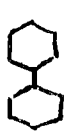
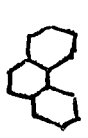
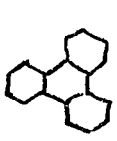
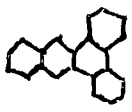
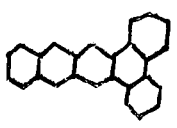
The C_{2v} programme has been used for calculations on molecules mPn where $-1 \leqslant m \leqslant 3$, $2 \leqslant n \leqslant 5$. i.e. the molecules considered as L fragments have been diphenyl, phenanthrene, triphenylene, 1.2, 3.4-dibenzanthracene and 1.2, 3.4-dibenz tetracene and those as R fragments

naphthalene, anthracene, tetracene and pentacene. The highest occupied orbital of every acene is antisymmetric with respect to reflection in the plane of symmetry including the z-axis, and so are those of diphenyl, 1.2, 3.4-dibenz-anthracene and 1.2, 3.4-dibenztetracene. Molecules compounded of these may reasonably be considered by the present method using only four configurations, one of each type. Molecules where L is triphenylene which has a degenerate pair of top occupied orbitals or phenanthrene whose top orbital is symmetric require more configurations, some of which will have the symmetry of the ground state and so will lower its energy. For these molecules 12 configurations have been considered, being the three lowest of each type. The results of these calculations are tabulated in Table III.1. For consistency we have quoted only those calculated assuming the electron affinities of acceptor orbitals to be zero. Calculations using Hedges and Matsen's (1958) values were done for the molecules 2Pn and 3Pn and gave results which agreed with those quoted to within $10cm^{-1}$.

TABLE III.1

p-bands calculated by Longuet-Higgins/Murrell method (cm^{-1})

For each molecule is given the predicted transition energy and the type of the dominant configuration in the excited state with its coefficient in the configurational eigenvector.

m	L	n = 2	3	4	5
		R				
-1		33506 RR*.895	26052 RR*.979	20863 RR*.971	17131 RR*.995
0		32208 LL*.717	25900 RR*.964	21083 RR*.982	17335 RR*.991
1		35431 RR*.831	27234 RR*.989	21191 RR*.994	17354 RR*.997
2		28570 LL*.998	26654 RR*.998	21190 RR*.991	17328 RR*.9996
3		22648 LL*.9995	22653 LL*.9996	21204 RR*.9989	17338 RR*.9998

The spectra observed by Clar together with the experimental values for the fragments which were used in the present calculations are shown in Table III.2.

TABLE III.2

Experimental p-band frequencies

(Pyrene benzologues from Clar 1960, 1962, 1963, others from Matsen 1956)

	n	2	3	4	5
	ν_p (fragment)	35090	26700	21220	17345
m	ν_p (fragment)				
-1	37350	28650	22650	18570	-
0	34210	28990	22650	18730	-
1	35170	29330	22780	-	-
2	28640	29240	22780	-	-
3	22670	22780	22620	-	-

A study of Tables III.1 and III.2 shows that, while the qualitative feature of an asymmetric annelation effect is reproduced by the present method the quantitative predictions are not very satisfactory.

Calculations on molecules 2P2 and 3P3 using the D_{2h} programme (i.e. considering these molecules as diphenyl with two naphthalenes or anthracenes joined to it) give the results 31280 cm^{-1}, 19725 cm^{-1} respectively.

In the majority of the calculations the predicted excited state is found to resemble far too closely the locally excited configuration of the dominant fragment and consequently the transition energy is little different from that of this fragment. Experimentally we see that the transition is shifted considerably to lower frequencies and so we may conclude that our model does not introduce sufficient interaction between the configurations. Changes in the numerical values used as data would have to be

unrealistic to produce better answers and anyway no theoretically justifiable way of making such changes is apparent.

Regretfully we conclude that the method is not suitable for these molecules.

6. Discussion of predictions by the Hückel method of p-band frequencies for these molecules.

The results of the Hückel calculations for the top occupied orbital in the benzologues of pyrene and some related molecules are given in Table III.3. Also given are the results of calculations by Goodwin and Morton-Blake (1963-64) which by means of somewhat arbitrary variations of resonance integrals, give a slightly better linear correlation with the observed frequencies.

The predicted frequencies are of two types: first those calculated from the linear relation proposed by Murrell (1963)

$$\nu\ (cm^{-1}) = 21940\,\Delta m + 8200 \qquad (3.25)$$

which was derived as the best straight line to fit experimental data for cata-condensed benzenoid hydrocarbons with up to 5 rings; (a similar relation based on a different selection of molecules is given by Streitwieser (1961).

$$\nu\ (cm^{-1}) = 19020\,\Delta m + 10520 \qquad (3.26)$$

predictions using this are about equally as good as those using (3.25)). Second, those derived from the best straight line (least squares deviations) for those molecules of the present series for which the spectra have been observed.

TABLE III.3

Molecule	Observed p-band	Calculated from Hückel Murrell's line	Calculated from Hückel Best st. line	Goodwin and Morton-Blake Murrell	Goodwin and Morton-Blake Best
-1P0	34190	34760	33700	-	-
0P0	29990	27730	27290		
-1P1	35210	38220	36870	41070	-
0P0	30170	30010	29370	-	-
1P1	30400	30580	31690	-	-
-1P2	28650	30100	29450	30840	29100
0P2	28990	30370	29700	30880	29140
1P2	29330	30180	29530	30790	29050
2P2	29240	29090	28530	30650	28920
-1P3	22650	23810	23700	24260	22720
0P3	22620	23940	23830	24270	22730
1P3	22780	23870	23760	24250	22710
2P3	22780	23770	23670	24240	22700
3P3	22620	23080	23040	24124	22590
-1P4	18570	19700	19950	19960	18550
0P4	18730	19790	20040	-	-
1P4	-	19740	-	-	-
2P4	-	19710	-	-	-
3P4	-	19650	-	-	-
-1P5	-	16960	-	-	-
0P5	-	17020	-	-	-
1P5	-	16990	-	-	-
a1.P.0	26010	24340	24320	-	-
a1.P.c1	22170	23210	23160	-	-
a1.Pd1	21830	21480	21580	-	-
a2.P.0	22830	21480	21580	-	-
a2.P.c1	22830	21230	21350	-	-
a2.P.d1	19380	19210	19800	-	-
a2.P.c2	22120	20199	20410	-	-
a2.P.d2	17360	17550	17784	-	-

The lines used for these were:

HMO results: $\nu\,(cm^{-1}) = 20041\,\Delta m + 9448$ (3.27)

Goodwin/Morton-Blake: $\nu\,(cm^{-1}) = 21283\,\Delta m + 7142$ (3.28)

A comparative test on the two methods with the 10 molecules for which both methods have been used showed a mean square deviation from a straight line five times greater for the HMO method than for the Goodwin/Morton-Blake method.

All the qualitative features which Clar discusses under the heading of annelation effects are satisfactorily predicted by both these methods; especially the asymmetric annelation effects in the molecules mPn and the differences between the molecules am.P.cn and am.P.dn. It is apparent that the simple Hückel method is quite adequate for these predicitions and often gives good quantitative predictions also. It is not clear what advantage (other than slightly better numerical answers) may be obtained by using the methods of Goodwin and Morton-Blake which, like the qualitative ideas of Clar, involve several arbitrary choices of resonance integrals, and other choices requiring much chemical intuition.

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CHAPTER IV

THE EFFECTS ON π-ELECTRON ENERGY OF THE FORMATION OF VACANCIES IN A GRAPHITE LAYER

1. Introduction

The crystal structure of graphite consists of layers of carbon atoms in a hexagonal array separated by distances of the order of 3.4Å, the bonds in the layers being 1.42Å long. When graphite is irradiated by neutrons (as in a nuclear reactor) two of the many observed physical changes are an expansion and an increase in internal energy. A bibliography of this topic is given by Coulson, Herraez, Leal, Santos and Senent (1963).

The formation of vacancies - where a carbon atom is removed from its site in the lattice and settles elsewhere, often between layers, is a mechanism which explains the physical observations and it is of interest to calculate the energy required to form such a vacancy. An absolute calculation is not possible as too many quantities are involved (see section 7 below), but it is feasible to compare two alternative models of the vacancy. The first assumes the expulsion of a single carbon atom with its π-electron, with no subsequent change in the neighbours to the vacancy other than a possible interaction between the three σ-orbitals on the atoms adjacent to the vacancy.

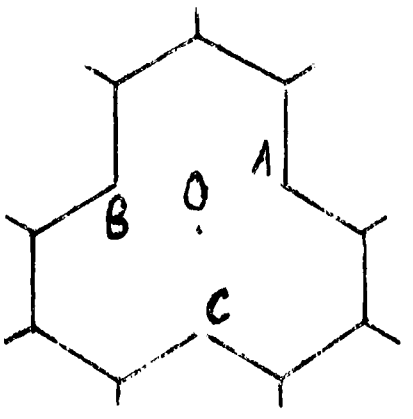


Fig. 1 A vacancy and its neighbours

The second supposes that the atoms adjacent to the vacancy (A, B, C in fig. 1) change their hybridization from $sp^2\pi$ to s^2p^2 with various consequent energy changes described in section 7 below. The chief term of the difference in formation energy between the two models is the difference in the change of π-energy. The calculations to be described in the present chapter estimate this difference using the HMO method to compute the π-energy. Calculations are also reported on the energy required to form a divacancy (two adjacent vacancies).

The π-energy changes correspond to the loss of one or four atoms with their π-electrons from the system respectively. It was hoped that a good estimate of these energy changes might have been obtained by considering relatively small fragments of the layer with vacancies at their centres and observing how the loss of energy approached a limit as the size of these fragments was increased. This was found not to give very reliable results as the energies obtained varied according to certain details of the geometry of the molecule, and it was necessary to consider fairly large fragments.

2. Method of calculation - D_{3h} symmetry

In order to be able to make maximum use of molecular symmetry fragments were first considered which had trigonal (D_{3h}) symmetry. Since the π-orbitals with which we are concerned are antisymmetric with respect to reflection in the plane of the fragment we need only consider the symmetry operations of the point group C_{3v}. This group is considered very fully by Altmann (1962) and the majority of what follows is a direct application of the methods given there.*

---

* I should like also to acknowledge some conversations with Dr. Altmann which helped considerably to clarify these ideas in my mind.

TABLE IV.1 is a character table for this group (Altmann 1962, p.178)

C_{3v}	E	3σ	$2C_3$
A_1	1	1	1
A_2	1	-1	1
E	2	0	-1

TABLE IV.1 Character table for C_{3v}

Fig 2 shows a small fragment with the disposition of the symmetry elements and the cartesian axes.

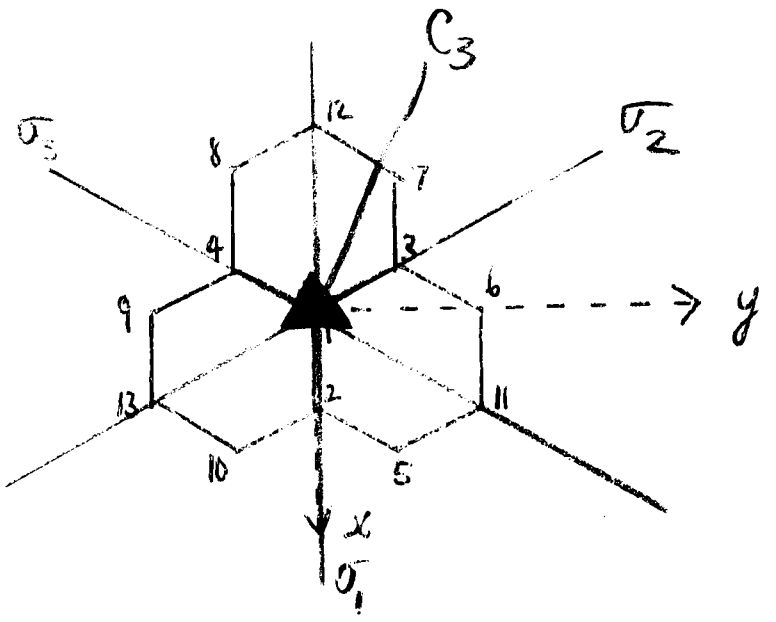


Fig. 2

In order to make use of symmetry to simplify the secular determinant for fragments of this shape we may use symmetrizing or projection operators on the atomic orbitals (basis functions) in order to generate linear combinations which transform as the irreducible representations of the group. We shall demonstrate how this is done for a set of six atoms (e.g. 5, 6, 7, 8, 9 and 10 in fig. 2) related to one another by the symmetry elements. We shall then show how these functions are modified when an atom lies on a plane of symmetry.

First we consider the effect of each of the symmetry operators acting on the functions, which here are atomic 2pπ orbitals and so may be considered as polar vectors normal to the molecular plane located at the numbered sites of fig.1. In doing this we use the passive convention for rotations, i.e. we consider the operation C_3^+ to be a counterclockwise rotation of the axes relative to a fixed molecule or (often easier to visualize) a clockwise rotation of the points relative to the axes.

In Table IV.2 we write, for short, atom numbers when we mean π-orbitals on those atoms.

	transformed into by operation R					
atomic π-orbital	R = E	σ_1	σ_2	σ_3	C_3^+	C_3^-
5	5	10	8	6	9	7
6	6	9	7	5	10	8
7	7	8	6	10	5	9
8	8	7	5	9	6	10
9	9	6	10	8	7	5
10	10	5	9	7	8	6
χ	6	0	0	0	0	0

Table IV.2 Transformation of atomic orbitals by operations of the group C_{3v}

The final line of Table IV.2 gives the number of orbitals of the set {5, ... 10} which are invariant under each operation and is equal to the character of that operation in the reducible representation spanned by the set of functions {5, ... 10}. By inspection we may see that

$$\chi\{5, \ldots 10\} = \chi^{A_1} + \chi^{A_2} + 2\chi^{E} \qquad (1.1)$$

We thus see that each set of six functions such as $\{5,\ldots 10\}$ may be resolved into one linear combination belonging to A_1, one belonging to A_2 and two pairs belonging to E. Those belonging to E may be divided further into two non-interacting sets belonging respectively to the two columns of a matrix representation of E. A convenient representation to use is that with basis $<x, y|$, as this leads to real linear combinations; (for some applications complex combinations belonging to columns of the representation with basis $<x + iy, x - iy|$ are useful, but here, where we are only concerned with energies, real orbitals are to be preferred). This representation is given by Altmann (1962, p.106 but wrongly transcribed on p.148) and is repeated in Table IV.3.

E	σ_1	σ_2	σ_3	C_3^+	C_3^-
$\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}$	$\begin{bmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & \frac{1}{2}\end{bmatrix}$	$\begin{bmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & \frac{1}{2}\end{bmatrix}$	$\begin{bmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{bmatrix}$	$\begin{bmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{bmatrix}$

Table IV.3 The E representation of C_{3v} with basis $<x, y|$

In order to generate the symmetry adapted basis functions we apply the operators:

$$W^j_{s,t} = \sum_{r \epsilon G} D^j(R)^*_{s,t} \; R \qquad (1.2)$$

where R are the operators of the group G and $D^j(R)^*_{s,t}$ are the complex conjugates of the matrix elements of these operations in the irreducible representation j. For the one-dimensional representation the characters are the matrix elements; for the two dimensional E representation linearly independent functions are obtained by taking the elements

Table IV.4 Symmetrizing and projection operators C_{3v} - effect of the W^i_{ts} on the atomic orbitals ϕ_5-ϕ_{10}

At each position in the table is given the function as derived according to the definition of W^i_{ts}, together with its expression in terms of the orthonormal functions a_1, a_2, e_1 - e_4.

op. \ atomic orbital	5	6	7	8	9	10
W^{A_1}	$5+10+8+6+9+7$ $\sqrt{6}a_1$	$6+9+7+5+10+8$ $\sqrt{6}a_1$	$7+8+6+10+5+9$ $\sqrt{6}a_1$	$8+7+5+9+6+10$ $\sqrt{6}a_1$	$9+6+10+8+7+5$ $\sqrt{6}a_1$	$10+5+9+7+8+6$ $\sqrt{6}a_1$
W^{A_2}	$5-10-8-6+9+7$ $\sqrt{6}a_2$	$6-9-7-5+10+8$ $-\sqrt{6}a_2$	$7-8-6-10+5+9$ $\sqrt{6}a_2$	$8-7-5-9+6+10$ $-\sqrt{6}a_2$	$9-6-10-8+7+5$ $\sqrt{6}a_2$	$10-5-9-7+8+6$ $-\sqrt{6}a_2$
W^{E}_{11}	$5+10-\frac{1}{2}(8+6+9+7)$ $\sqrt{3}e_1$	$6+9-\frac{1}{2}(7+5+10+8)$ $\frac{1}{2}(-\sqrt{3}e_1+3e_2)$	$7+8-\frac{1}{2}(6+10+5+9)$ $\frac{1}{2}(-\sqrt{3}e_1-3e_2)$	$8+7-\frac{1}{2}(5+9+6+10)$ $\frac{1}{2}(-\sqrt{3}e_1-3e_2)$	$9+6-\frac{1}{2}(10+8+7+5)$ $\frac{1}{2}(-\sqrt{3}e_1+3e_2)$	$10+5-\frac{1}{2}(9+7+8+6)$ $\sqrt{3}e_1$
W^{E}_{12}	$\frac{1}{2}\sqrt{3}(-8+6+9-7)$ $\sqrt{3}e_2$	$\frac{1}{2}\sqrt{3}(-7+5+10-8)$ $\frac{1}{2}(3e_1+\sqrt{3}e_2)$	$\frac{1}{2}\sqrt{3}(-6+10+5-9)$ $\frac{1}{2}(3e_1-\sqrt{3}e_2)$	$\frac{1}{2}\sqrt{3}(-5+9+6-10)$ $\frac{1}{2}(-3e_1+\sqrt{3}e_2)$	$\frac{1}{2}\sqrt{3}(-10+8+7-5)$ $\frac{1}{2}(-3e_1-\sqrt{3}e_2)$	$\frac{1}{2}\sqrt{3}(-9+7+8-6)$ $-\sqrt{3}e_2$
W^{E}_{21}	$\frac{1}{2}\sqrt{3}(-8+6-9+7)$ $\sqrt{3}e_4$	$\frac{1}{2}\sqrt{3}(-7+5-10+8)$ $\frac{1}{2}(3e_3-\sqrt{3}e_4)$	$\frac{1}{2}\sqrt{3}(-6+10-5+9)$ $\frac{1}{2}(-3e_3-\sqrt{3}e_4)$	$\frac{1}{2}\sqrt{3}(-5+9-6+10)$ $\frac{1}{2}(-3e_3-\sqrt{3}e_4)$	$\frac{1}{2}\sqrt{3}(-10+8-7+5)$ $\frac{1}{2}(-3e_3+\sqrt{3}e_4)$	$\frac{1}{2}\sqrt{3}(-9+7-8+6)$ $\sqrt{3}e_4$
W^{E}_{22}	$5-10+\frac{1}{2}(8+6-9-7)$ $\sqrt{3}e_3$	$6-9+\frac{1}{2}(7+5-10-8)$ $\frac{1}{2}(\sqrt{3}e_3+3e_4)$	$7-8+\frac{1}{2}(6+10-5-9)$ $\frac{1}{2}(-\sqrt{3}e_3+3e_4)$	$8-7+\frac{1}{2}(5+9-6-10)$ $\frac{1}{2}(\sqrt{3}e_3-3e_4)$	$9-6+\frac{1}{2}(10+8-7-5)$ $\frac{1}{2}(-\sqrt{3}e_3-3e_4)$	$10-5+\frac{1}{2}(9+7-8-6)$ $-\sqrt{3}e_3$
V^{E}	$2(5)-9-7$ $\sqrt{3}(e_1+e_3)$	$2(6)-10-8$ $\frac{1}{2}(-\sqrt{3}e_1+3e_2+\sqrt{3}e_3+3e_4)$	$2(7)-5-9$ $\frac{1}{2}(-\sqrt{3}e_1-3e_2-\sqrt{3}e_3+3e_4)$	$2(8)-6-10$ $\frac{1}{2}(-\sqrt{3}e_1-3e_2+\sqrt{3}e_3-3e_4)$	$2(9)-7-5$ $\frac{1}{2}(-\sqrt{3}e_1+3e_2-\sqrt{3}e_3-3e_4)$	$2(10)-8-6$ $\sqrt{3}(e_1-e_3)$

$a_1 = \frac{1}{\sqrt{6}}(5+6+7+8+9+10)$ $\quad e_1 = \frac{1}{\sqrt{3}}((5+10)-\frac{1}{2}(6+7+8+9))$

$a_2 = \frac{1}{\sqrt{6}}(5-6+7-8+9-10)$ $\quad e_2 = \frac{1}{2}(6-7-8+9)$

} S in σ_1

$e_3 = \frac{1}{\sqrt{3}}((5-10)+\frac{1}{2}(6-7+8-9))$

$e_4 = \frac{1}{2}(6+7-8-9)$

} A in σ_1

from different rows of the matrix representatives of table IV.3. Table IV.4, which shows the result of applying each of the six operators to each of the six atomic orbitals, shows how this occurs. Also given is the result of applying the operator $V^E = \sum_{R \in G} \chi^E(R)^* R$ using only the characters of the E representations.

It will be seen that the operators W^{A_1} and W^{A_2} give rise to one function each (remember that numerical factors have no significance when constructing linear combinations like these) and that the operators $W^E_{s,t}$ and V^E give combinations of four linearly independent symmetry-adapted functions e_i. All functions generated by W^E_{11} and W^E_{12} may be expressed as combinations of e_1 and e_2 (e_1 is chosen arbitrarily, e_2 to be orthogonal to e_1) and are symmetric with respect to reflection in σ_1 (this plane rather than the others because of the choice of basis - they have the symmetry of x). Functions generated by W^E_{21} and W^E_{22} are combinations of e_3 and e_4 and are antisymmetric with respect to reflection in σ_1 (like y).

Note further that the use of the operators $W^E_{s,t}$ has led to all the orthogonal functions e_1, e_2, e_3 and e_4 directly. Use only of W_{11} and W_{22} (the projection operators) would have given e_1 and two combinations of e_1 and e_2 which could have been subtracted to give e_2, etc. However, the use of V^E would have given rather complicated combinations from which it would have been possible (but liable to give rise to slips in practice) to derive two non-interacting sets of functions. The use of the operators $W^i_{t,s}$ in cases like this where a suitable representation is readily available is thus strongly recommended.

The functions analogous to a_1, a_2, e_{1-4} when the typical atom lies on σ_1 are given in Table IV.5. The set {2, 3, 4} has the typical atom on the +x axis and the set {11, 12, 13} has it on the -x axis.

TABLE IV.5

Linear combinations of sets of 3 atoms

	(3)+function	(3)-functions
a_1	$\frac{1}{\sqrt{3}}(2 + 3 + 4)$	$\frac{1}{\sqrt{3}}(11 + 12 + 13)$
a_2	-	-
e_1	$\frac{1}{\sqrt{6}}(2(2) - 3 - 4)$	$\frac{1}{\sqrt{6}}(11 + 13 - 2(12))$
e_2	-	
e_3	-	$\frac{1}{\sqrt{2}}(11 - 13)$
e_4	$\frac{1}{\sqrt{2}}(3 - 4)$	

The symmetrized basis functions are thus of 13 different kinds which we shall name according to the symmetry and the number of atomic orbitals from which they are derived. They are:

$a_1^{(1)}$, $a_1^{(3)+}$, $a_1^{(3)-}$, $a_1^{(6)}$; $a_2^{(6)}$; $e_1^{(3)+}$, $e_1^{(3)-}$, $e_1^{(6)}$, $e_2^{(6)}$; $e_3^{(6)}$, $e_4^{(3)+}$, $e_4^{(3)-}$, $e_4^{(6)}$.

The bracketed superscript indicates the number of atomic orbitals from which the function is derived; the + and - indicate whether the typical atom of a set of 3 is on the + or - x-axis, respectively.

The secular determinant may be divided into four determinants each including functions of all kinds between semicolons in the above list. The values of the matrix elements between these kinds of functions when the corresponding sets of atoms are joined by sets of bonds

TABLE IV.6

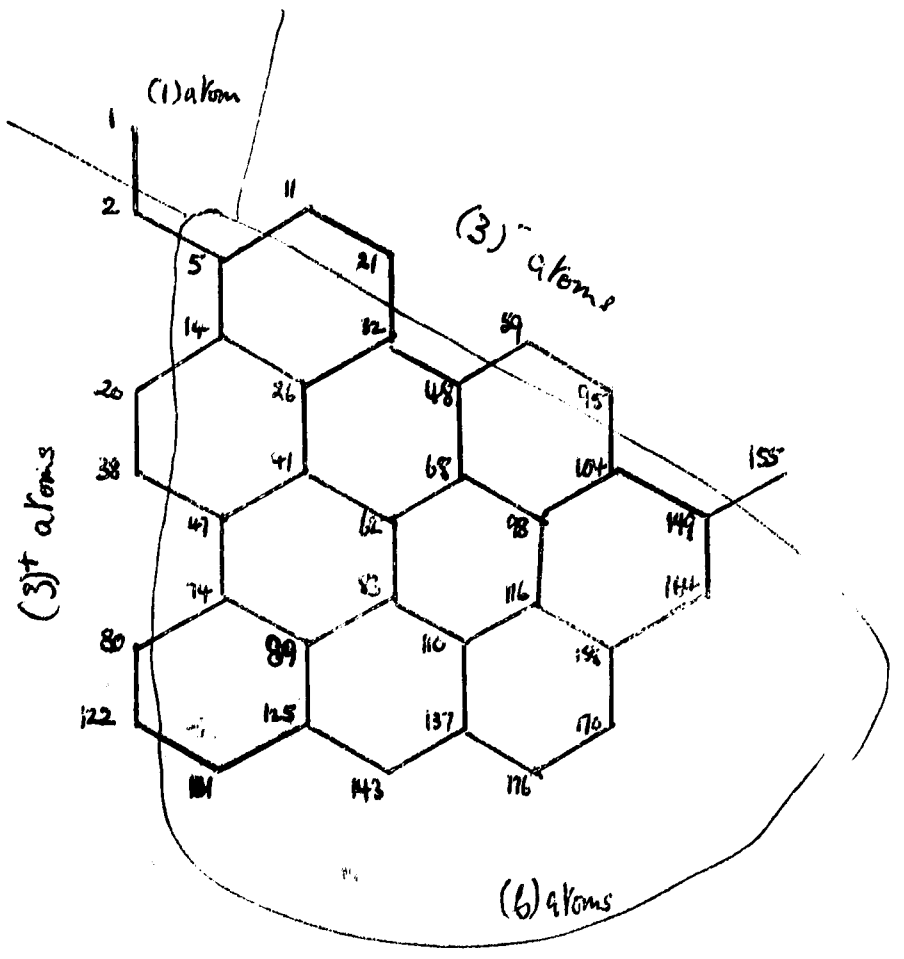
Matrix Elements

$\langle a_1^{(1)} \vert H \vert a_1^{(3)+} \rangle = \sqrt{3}$			
$\langle a_1^{(3)\pm} \vert H \vert a_1^{(3)\pm} \rangle$	$= \langle e_1^{(3)\pm} \vert H \vert e_1^{(3)\pm} \rangle$	$= \langle e_3^{(3)\pm} \vert H \vert e_3^{(3)\pm} \rangle$	$= 1$
$\langle a_1^{(3)\pm} \vert H \vert a_1^{(6)} \rangle$	$= \langle e_1^{(3)+} \vert H \vert e_1^{(6)} \rangle$	$= \langle e_4^{(3)+} \vert H \vert e_4^{(6)} \rangle$	$= \sqrt{2}$
	$\langle e_1^{(3)-} \vert H \vert e_1^{(6)} \rangle$	$= \langle e_4^{(3)-} \vert H \vert e_4^{(6)} \rangle$	$= \frac{1}{\sqrt{2}}$
	$\langle e_1^{(3)-} \vert H \vert e_2^{(6)} \rangle$	$= \langle e_4^{(3)-} \vert H \vert e_3^{(6)} \rangle$	$= \sqrt{\frac{3}{2}}$
$\langle a_1^{(6)} \vert H \vert a_1^{(6)} \rangle$			
$= \langle a_2^{(6)} \vert H \vert a_2^{(6)} \rangle$	$= \langle e_1^{(6)} \vert H \vert e_1^{(6)} \rangle$	$= \langle e_3^{(6)} \vert H \vert e_1^{(6)} \rangle$	$= 1$
	$\langle e_2^{(6)} \vert H \vert e_2^{(6)} \rangle$	$= \langle e_4^{(6)} \vert H \vert e_4^{(6)} \rangle$	$= 1$

Where $\pm$ signs occur either the two upper or the two lower signs should be taken. Other possible matrix elements are either identically zero or cannot occur in molecules of the type under consideration.

are given in Table IV.6 (the unit is the C-C resonance integral β)

The secular matrices A_1, A_2, $E_{1,2}$ and $E_{3,4}$ may be easily constructed by considering a 60° sector (see Fig. 2a) of the complete graphite fragment and choosing appropriate matrix elements from table IV.6.



Numbering is that used to include every atom of the fragment

Fig. 2a

In order to calculate the loss of π-energy when atom 1 is removed it is seen to be necessary only to solve A_1 matrices for the cases with and without the $a_1^{(1)}$ function for atom 1. However if we wish to consider the fragments where atoms 1, 2, 3, 4 are removed from the conjugation we must solve also the E matrices with and without the $e_1^{(3)+}$, $e_3^{(3)+}$ functions for atoms 2, 3, 4. Note that if we are concerned solely with differences in π-electron energy we need never consider the A_2 matrix. A programme to carry out these calculations has been written and used for some of the larger fragments.

3. Results - D_{3h} Symmetry

Before the method described above for maximum reduction of the secular determinants had been fully worked out, calculations were done on fragments with D_{3h} symmetry, but making use only of the plane of symmetry including atoms 1 and 2. i.e. assuming only C_{2v} symmetry. Fig. 3 shows the largest fragment considered in this way. The

numbers in the rings indicate which rings are present at each stage of the calculation. (e.g. calculation no.7 is for a fragment including all rings with no. $\leq$ 7.)

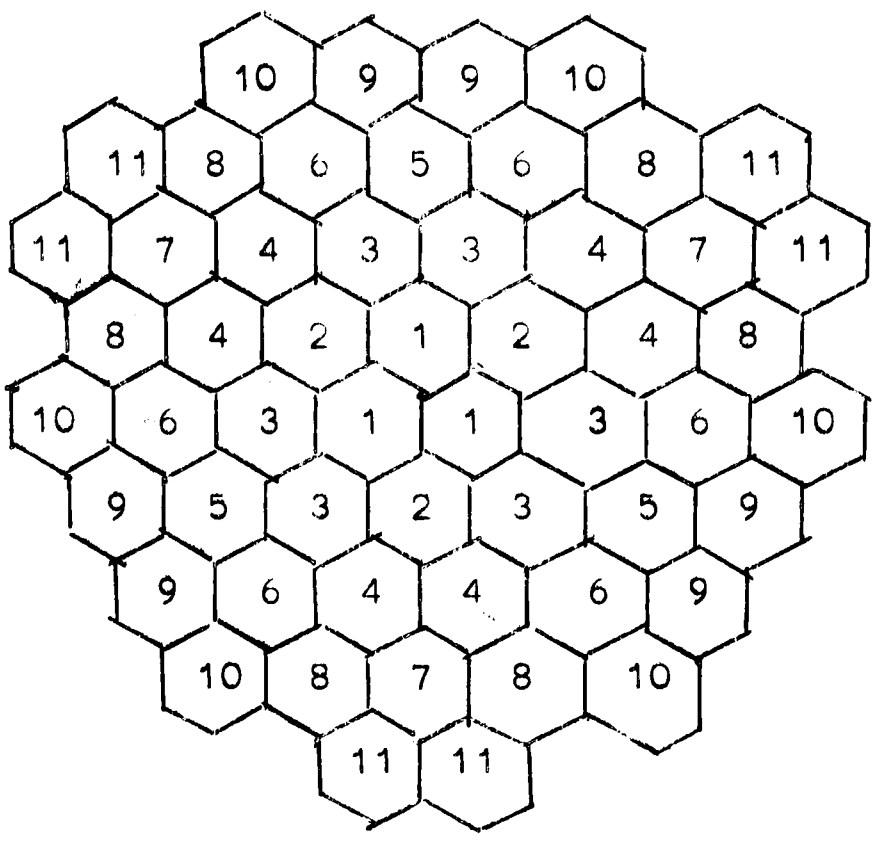


Fig.3

For each of the 11 fragments all positive eigenvalues were calculated. (Since β is negative these are the occupied levels). The total π-energy for the original fragments, the fragments less the central atom and the fragments less the central 4 atoms together with their differences are tabulated in Tables IV.7 and IV.7a (the energy unit is β). Calculations nos. 2, 4, and 8 for the 'O-1' energy were done independently by Herraez and Senent (Coulson et. al 1963) and, on the basis of these three values only, they fitted an extrapolation formula

$$\Delta E_{\pi} = \frac{n}{an + b}\,\beta$$

from which they obtained $\Delta E_{\pi}(n = \infty) = 2.75\beta$. In view of the somewhat variable values for ΔE_{π} obtained in some of the other calculations of the present series, this extrapolation seems of doubtful validity. (It must be noted however, that the answer 2.75β is identical to that

obtained independently by a completely different method by Coulson and Koutecký (1963)).

Calculation No.	Original Fragment Rings	Atoms(n)	Total π-energy 0	−1	−4
1	3	13	17.827	14.928	8.485
2	6	22	30.810	27.885	23.035
3	12	37	53.887	51.470	45.049
4	18	52	76.335	73.485	68.372
5	21	61	90.229	87.404	81.484
6	27	73	108.621	105.832	99.903
7	30	82	122.131	113.341	113.940
8	36	94	140.522	137.727	132.280
9	42	109	163.873	161.392	155.279
10	48	121	182.008	179.531	173.473
11	54	136	205.176	202.489	197.039

Table IV.7 π-Energy of fragments with D_{3h} symmetry

A preliminary glance at Table IV.7a shows that the largest discrepancies from a smooth variation of ΔE_π occur at the $E_r^{(1)}$ energy in calculations nos. 3, 9, 10. These give an unexpectedly low value. These three fragments are those which have both an even number of rings and an odd number of atoms. When the molecular orbital energies themselves are studied it is found that the critical fact is the number of non-bonding orbitals in the fragment; this number is very dependent on details of shape and numbers of atoms and all the observed inequalities may be correlated with it.

The relationship between existence of non-bonding molecular orbitals, (NBMOs) and consequent instability, and the possibility of drawing Kekulé structures has been

discussed fully by Longuet-Higgins (1950) and by Dewar and Longuet-Higgins (1952). The chief result of their work which is relevant to the present molecules is: The number of non-bonding molecular orbitals is equal at least to the number of carbon atoms lacking double bonds in a principal resonance structure. (A principal resonance structure is one which contains the greatest possible number of double bonds).

TABLE IV.7a

Loss of π-energy on removal of 1 and of 4 atoms from the layer

Calculation No.	Rings	Atoms(n)	Loss of π-energy* $E_r^{(1)}$	$E_r^{(4)}$
1	3	13	2.899	9.342
2	6	22	2.925	7.775
3	12	37	2.417	8.839
4	18	52	2.850	7.963
5	21	61	2.824	8.744
6	27	73	2.789	8.718
7	30	82	2.790	8.191
8	36	94	2.795	8.242
9	42	109	2.551	8.663
10	48	121	2.597	8.655
11	54	136	2.798	8.249
†12	60	148	2.791	8.299
13	63	157	2.787	8.647
14	69	169	2.768	8.640
15	75	181	2.760	8.632

* For definition of terms see Section 7.

† The last four rows of this table were computed by the method described in section 2 above. The results for smaller fragments were confirmed by this method.

In particular if we divide the atoms into two sets, starred and unstarred, in the usual way for **alternant** molecules, and the number of atoms in one set exceeds that in the other by m, there will be at least m non-bonding orbitals, as, any bond necessarily joining atoms of the two sets, these m atoms must be 'unpaired'.

The condition just mentioned is not the only cause of non-bonding orbitals (**cf.** cyclobutadiene discussed by Longuet-Higgins). If a molecule (like all fragments under consideration) with a plane of symmetry through a set of bonds, is such that the number of atoms on the plane of symmetry is even and the number of atoms on each side of the plane is odd, then the secular matrices corresponding to functions symmetric and antisymmetric with respect to the plane will both be odd and, having still the alternant property, will each have a zero eigenvalue. Such non-bonding orbitals are called <u>super numerary</u> by Longuet-Higgins. They may be connected with the presence of a ring of 4n (here n = 3) carbon atoms.

The numbers of non-bonding orbitals in the various fragments are shown in Table IV.8. The correlation of these with the calculated total π-energies is best displayed by plotting the π-energy per electron against the size of the fragment. (Fig 3a). For a molecule of infinite size this quantity tends to 1.576β (Coulson and Taylor 1952), and for smaller fragments it might be expected to tend monotonically towards this value from below. Most of the deviations from a smooth curve which appear in Fig. 3a correspond exactly to the variations in numbers of non-bonding orbitals. The fragments divide themselves naturally into two sets -

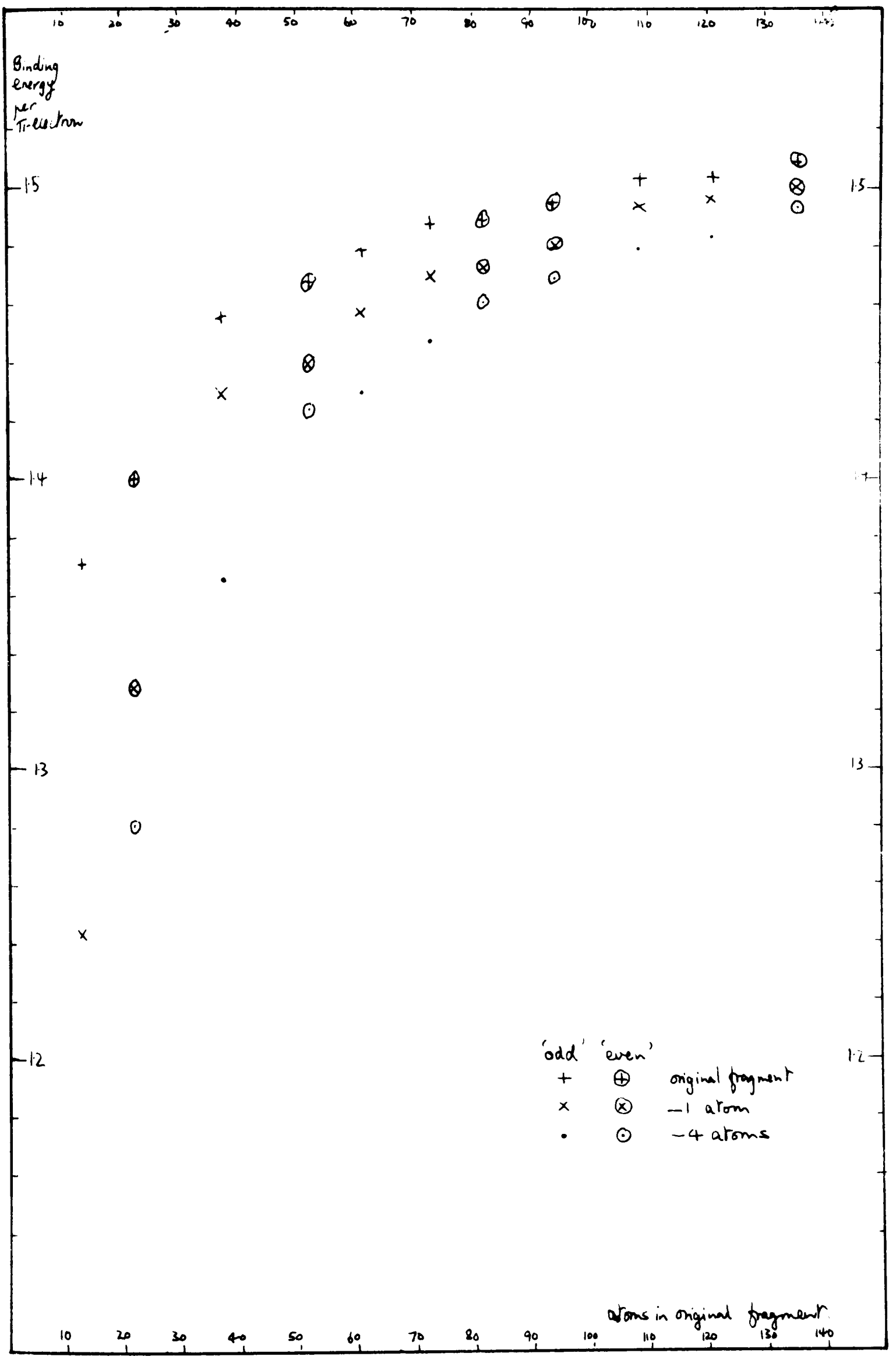


Fig 3a. D_{3h} fragments: Binding energy per π-electron.

those where the original fragment has an odd or an even number of atoms respectively. The former have 'high' total π-energy for the original fragment and the '-1' fragment and 'low' for the '-4' fragment; the latter the opposite. Fragments nos. 3, 9, 10 which have an anomalously low loss of energy on forming the '-1' fragment are those where non-excited Kekulé structures may be drawn for the '-1' fragment and there are no supernumerary NBMO's; hence these have greater stability than might otherwise be expected.

TABLE IV.8

Number of non-bonding molecular orbitals in fragments with D_{3h} symmetry

No.	Rings	Atoms	NBMO's Orig. fragment	'-1'	'-4'
1	3	13	1	2	3
2	6	22	2	3	0
3	12	37	1	0	3
4	18	52	2	3	0
5	21	61	1	2	3
6	27	73	1	2	3
7	30	82	2	3	0
8	36	94	2	3	0
9	42	109	1	0	3
10	48	121	1	0	3
11	54	136	2	3	0
12	60	148	2	3	0
13	63	157	1	2	3
14	69	169	1	2	3
15	75	181	1	2	3

4. Other odd fragments with C_{2v} symmetry

In order to confirm the suspected correlation with non-bonding orbitals further calculations have been done on a series of fragments with C_{2v} symmetry but constructed in such a way that the total number of atoms remains odd. This series, shown in Fig. 4, includes fragments nos. 1, 3 and 6 of the D_{3h} series.

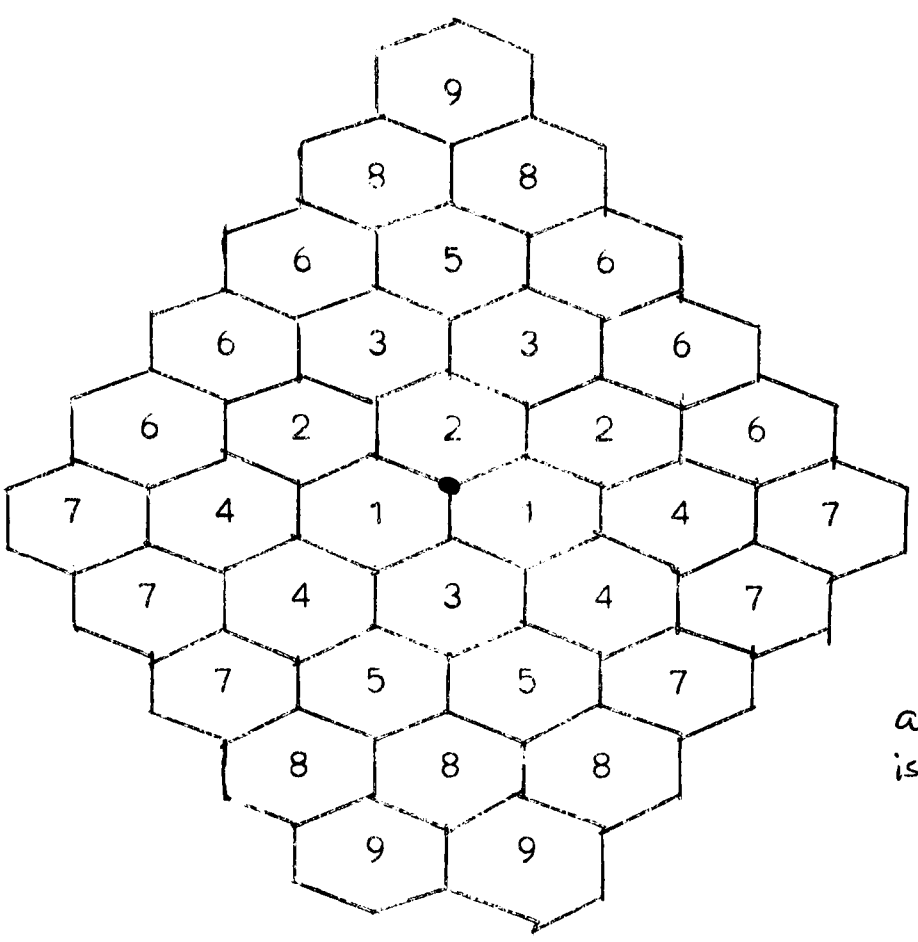


Fig. 4

The results of these calculations are given in Table IV.9

The anomalons ΔE's here correlate as expected with the non-bonding orbitals, the low values in the 0-1 column occurring where the -1 fragment is more stable than usual on account of having no NBMO's, and those in the 0-4 columns where the -4 fragment has 1 rather than 3 NBMO's. The NBMO's in the -4 fragments are all forced by the excess of atoms of one set; in the -1 fragments nos. 2, 3, 6 have this sort of NBMO; those in nos. 1, 5, 7, 9 are super-numerary.

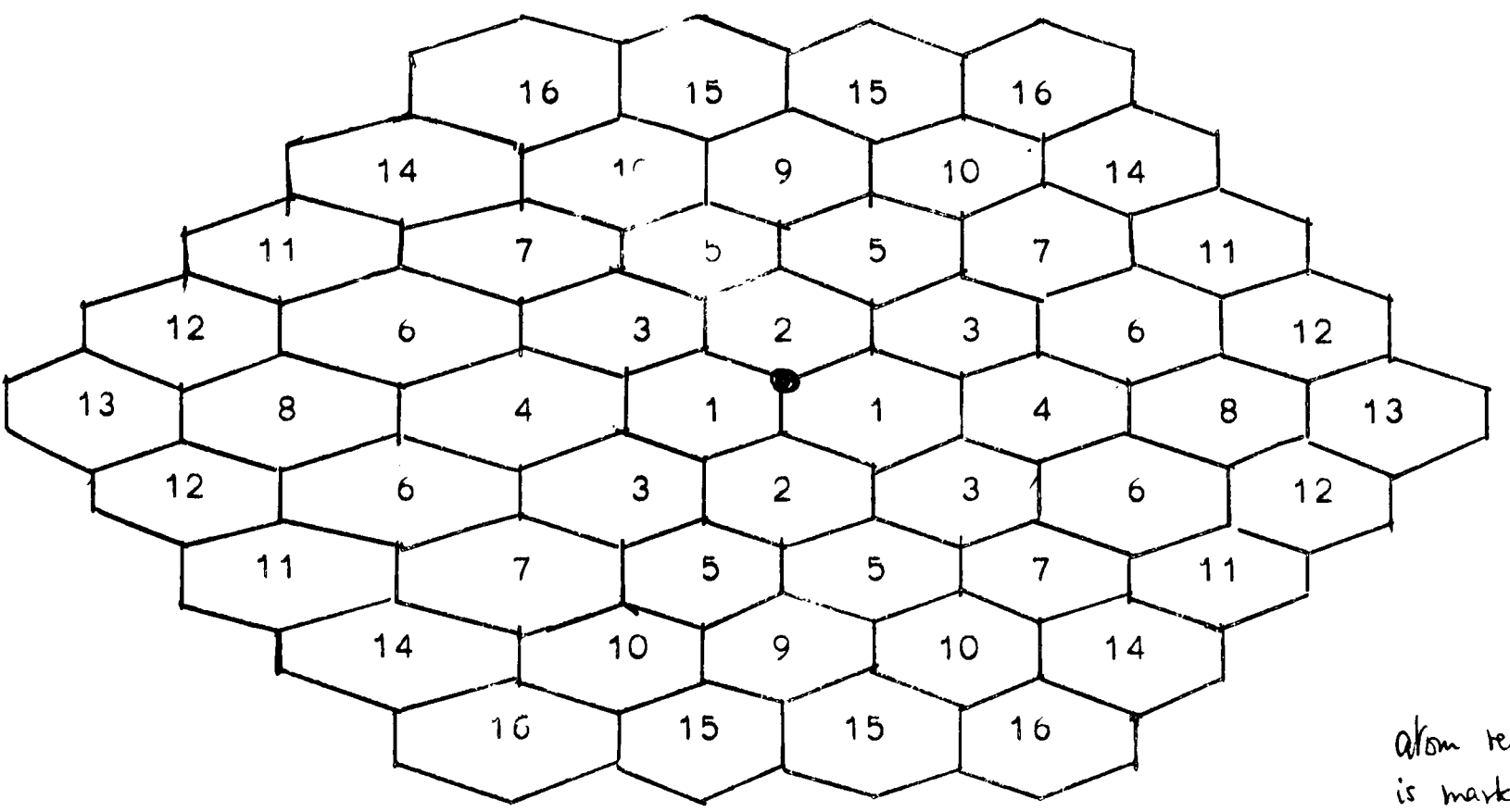
TABLE IV.9

Odd fragments with C_{2v} symmetry

rings	atoms	NBMO's			Loss of π-energy	
		0	-1	-4	$E_r^{(1)}$	$E_r^{(4)}$
1	3	13	1	2	3	2.899	9.342
2	5	19	1	2	1	2.916	8.390
3	8	27	1	2	1	2.880	8.278
4	12	37	1	0	3	2.417	8.839
5	15	45	1	2	3	2.745	8.742
6	21	59	1	2	1	2.829	8.319
7	27	73	1	2	3	2.789	8.718
8	30	85	1	0	3	2.603	8.675
9	33	93	1	2	3	2.695	8.568

5. Fragments with D_{2h} symmetry

In order to study the variation of $\triangle E_\pi$ in a series of fragments where the numbers of non-bonding orbitals do not vary so much from fragment to fragment a series of calculations were done on fragments with D_{2h} symmetry. The way these fragments are built up is shown in fig. 5.



atom removed is marked ●

Fig. 5

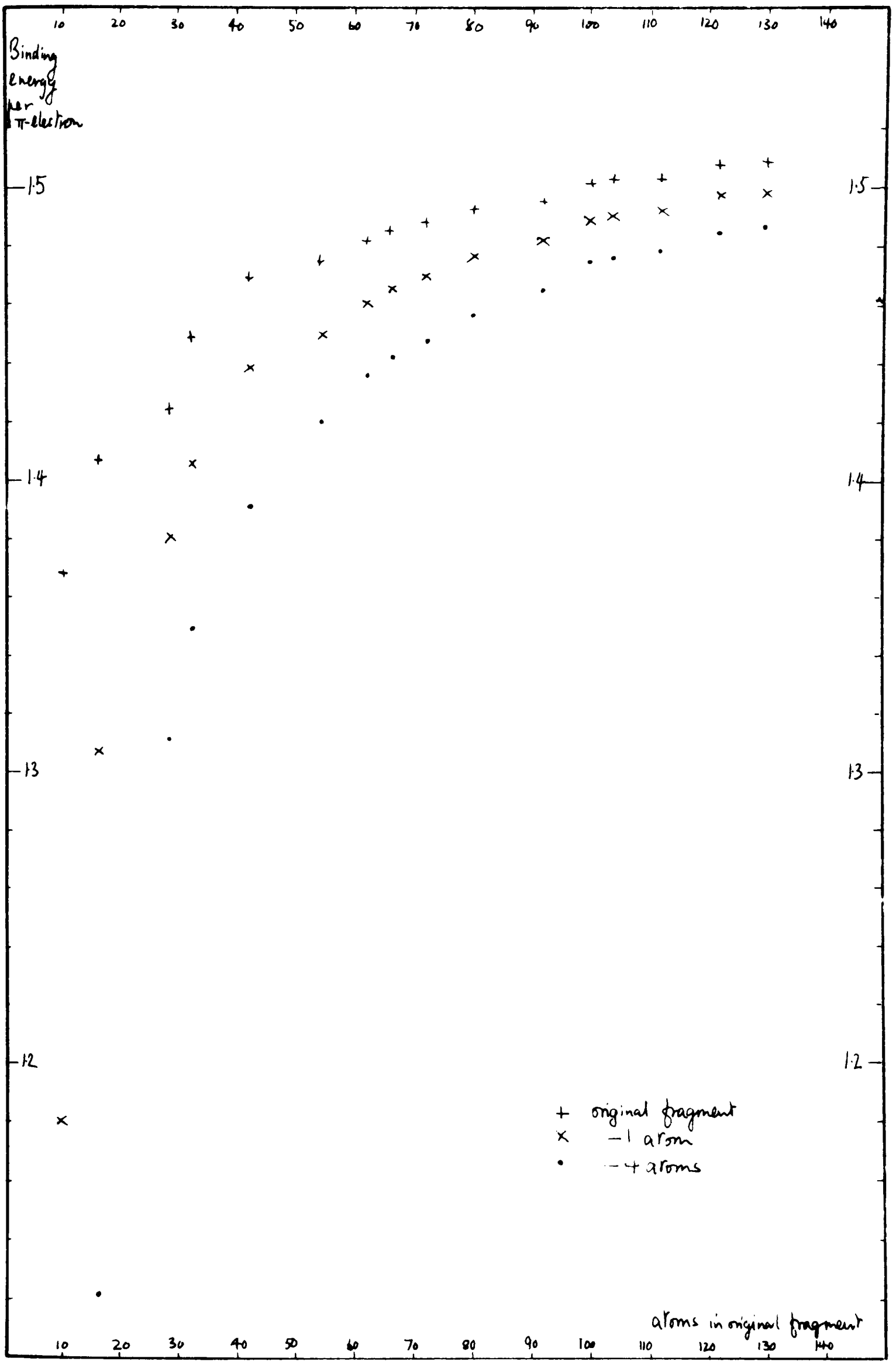


Fig 5a. D_{2h} fragments: Binding energy per π-electron

and the results of the calculations are given in Table IV.10. The binding energy per π-electron for these fragments is plotted in fig. 5a. The variation is here seen to be smoother than for the D_{3h} fragments, but it is not clear how best to make an extrapolation to infinite size for the energy differences. Hence we use the somewhat naive method of 'inspection' to give the following results:

Loss of π-energy on removal of a single atom from a layer of graphite = 2.75 ± 0.02 β

Loss of π-energy on removal of four atoms from the conjugation in a layer of graphite = 8.65 ± 0.04 β.

6. Formation of a divacancy

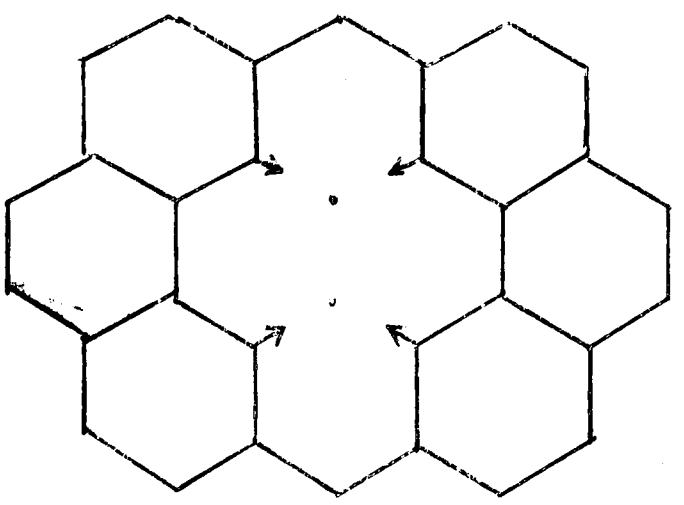


Fig. 6 Divacancy in D_{2h} fragment no. 4

The arrows denote singly occupied sp^2 hybrids on the four neighbour atoms to the divacancy.

The formation of a divacancy as in Fig. 6 involves the breaking of only five σ-bonds, compared with the six for two isolated vacancies. Such divacancies might thus be expected to be more stable and would tend to form preferentially. Consequently a calculation of the π-electron energy of such systems was thought worth-while. Calculations were done for the divacancies in all the D_{2h} fragments considered in section 4.

Calc.No.	Original fragment		Total π-energy			ΔE_π Loss of π-energy	
	Rings	atoms(n)	n-0	n-1	n-4	$E_r^{(1)}$	$E_r^{(4)}$
1	2	10	13.683	10.628	5.656	3.056	8.026
2	4	16	22.505	19.598	13.455	2.908	9.050
3	8	28	39.921	37.261	31.472	2.660	8.448
4	10	32	46.385	43.581	37.778	2.804	8.607
5	14	42	61.716	58.967	52.863	2.748	8.852
6	18	54	79.677	76.846	71.018	2.831	8.658
7	22	62	91.892	89.069	83.294	2.823	8.597
8	24	66	98.065	95.258	89.416	2.808	8.649
9	26	72	107.159	104.359	98.468	2.801	8.691
10	30	80	119.424	116.633	110.735	2.791	8.689
11	34	92	137.557	134.865	129.001	2.692	8.556
12	38	100	150.182	147.430	141.578	2.751	8.604
13	40	104	156.281	153.520	147.661	2.761	8.620
14	44	112	168.376	165.621	159.768	2.754	8.607
15	48	122	183.964	181.222	175.278	2.742	8.686
16	52	130	196.069	193.324	187.395	2.745	8.674

TABLE IV.10 Fragments with D_{2h} symmetry

The results of these calculations are given in Table IV.11 By 'inspection' we conclude that:

The loss of π-energy on formation of a divacancy in a layer of graphite = 4.52 ± 0.01β.

TABLE IV.11

Formation of a divacancy

calc.No.	π-energy n-2 atoms	loss of π-energy $E_r(2)$
1	8.944	4.739
2	17.970	4.530
3	35.361	4.560
4	41.832	4.553
5	57.209	4.507
6	75.138	4.538
7	87.356	4.536
8	93.532	4.533
9	102.633	4.526
10	114.899	4.525
11	133.032	4.525
12	145.656	4.526
13	151.755	4.526
14	163.849	4.527
15	179.447	4.517
16	191.550	4.519

7. Relation of these results to other energy quantities concerned with the formation of vacancies in graphite

A full discussion of the energy quantities concerned in the formation of vacancies in graphite has been made by Coulson (Coulson et. al. 1963, Coulson and Poole 1964). Here we give only a summary of the conclusions to show how the calculations described above fit in.

To do this we must define the following quantities.

$E_r^{(1)}$ the loss of π-energy when one atom is removed from the layer

$E_r^{(4)}$ the loss of π-energy when four atoms are removed from the layer

E_h energy to form a single vacancy when the neighbours do not change their hybridization and the ejected atom is put at the boundary of the layer

E_h' as E_h, but when the three neighbours to the vacancy change their hybridization from $sp^2\pi$ to s^2p^2

E_σ energy to break a C-C σ-bond without change of hybridization

E_σ' energy to break a C-C σ-bond when hybridization of one C atom is changed to s^2p^2

E_π π-electron binding energy per atom

E_c energy per atom of attraction and repulsion between layers.

E_{vs} energy of the $sp^2\pi$ valence state of carbon relative to the ^3P ground state.

E_{vs}' energy of the s^2p^2 valence state

E_v gain in energy due to interaction between the three singly occupied trigonal orbitals on atoms A,B,C.

E_v' energy of mutual repulsion between the atoms A, B, C, in s^2p^2 model

E_s heat of sublimation per atom of pure graphite.

Each of the above quantities is defined to be positive.

The following equalities may be shown to hold:

$$E_s = \frac{3}{2} E_\sigma + E_\pi + E_c - E_{vs} \qquad (7.1)$$

$$E_h = (3E_\sigma + E_r^{(1)} + 2E_c - E_v) - (E_{vs} + E_s) \qquad (7.2)$$

$$E_h' = (9E_\sigma - 6E_\sigma' + E_r^{(4)} + 2E_c + E_v' - 3E_{vs} + 3E_{vs}') - (E_{vs} + E_s) \qquad (7.3)$$

Subtracting (7.3) from (7.2) we get:

$$E_h - E_h' = (E_r^{(4)} - E_r^{(1)}) + 6(E_\sigma - E_\sigma') + (E_v + E_v') - 3(E_{vs} - E_{vs}') \qquad (7.4)$$

We have calculated the first term of the right hand side of 7.4. Using a value of -0.87 ev for β we get

$$E_r^{(4)} - E_r^{(1)} = (8.65 - 2.75)|\beta| = 5.1 \text{ eV} \qquad (7.5)$$

Basing the argument on calculations by Jordan and Longuet-Higgins (1962) it may be shown that:

$$0 \leqslant E_\sigma - E_\sigma' \leqslant 1.2 \text{ eV} \qquad (7.6)^{\dagger}$$

$$1.2 \leqslant E_{vs} - E_{vs}' \leqslant 3.9 \text{ eV} \qquad (7.7)$$

for all likely shapes of the vacancy region and so, as $E_v + E_v'$ is necessarily positive we conclude that $E_h - E_h'$ is positive and hence that the change of hybridization is energetically unfavourable. The numerical values are however not sufficiently well established absolutely to rule out the aternative model involving change of hybridization to s^2p^2.

7.1 Formation energy of a divacancy

We define three new energy quantities

E_{2h} **energy to form a divacancy (Fig. 6), the neighbours remaining in $sp^2\pi$ hybridization and the ejected atoms joining the edge of the layer.**

E_v'' **gain in energy due to interaction between the four singly occupied trigonal orbitals (shown by arrows in fig. 6).**

† These conditions are linked in that the lower values apply to the highest angle (120°) likely between the hybrids and the higher values apply to the lowest (103°).

$E_r^{(a)}$ loss of π-energy when two adjacent atoms are removed from the layer.

So we have:

$$E_{2h} = (5E_\sigma' + E_r^{(a)} + 4E_c - E_v'') - (2E_{vs} + 2E_s) \quad (7.8)$$

In order to compare the energy of a divacancy with that of two isolated vacancies treated by the first model we subtract twice equation (7.2) from (7.8).

$$E_{2h} - 2E_h = -E_\sigma + (E_r^{(a)} - 2E_r^{(1)}) - (E_v'' - 2E_v) \quad (7.9)$$

If we assume that E_v'' which represents two close interactions and four long ones is of similar magnitude to E_v which represents 3 close ones and that the magnitude of these is between 1 and 3 eV (Coulson, et al 1963) and further that E_σ is about 7eV, we have. using our calculated value of $0.98\beta = -0.85$eV for $(E_r^{(a)} - 2E_r^{(1)})$:

$$5 \leq E_{2h} - 2E_h \leq 7\text{eV} \quad (7.10)$$

We may thus safely conclude that it is energetically favourable for two vacancies to come together and form a divacancy.

References - Chapter IV

ALTMANN (1962) — Chapter 2 of 'Quantum Theory' Vol 2, Ed D. R. Bates, Academic Press, New York and London.

COULSON, HERRAEZ, LEAL, SAINTOS and SEHENT (1963) — Proc. Roy. Soc. A274, 461

COULSON and KOUTECKY (1964) — In course of publication.

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COULSON and TAYLOR (1952) — Proc. Phys. Soc. A65, 815.

DEWAR and LONGUET-HIGGINS (1952) — Proc. Roy. Soc. A214, 482.

JORDAN and LONGUET-HIGGINS (1962) — Mol. Phys. 5, 121.

LONGUET-HIGGINS (1950) — J. Chem. Phys. 18, 265.

Appendix A to Chapter I

Users' notes for the HMO Programmes.

These notes have been written as a self-contained description of the Programmes from the users' point of view. Consequently much is included which has already been said in Chapter I. It is regretted that its inclusion here does lead to duplication but this was thought to be more desirable than to omit certain rather arbitrarily chosensections.

In appendix I to this appendix (again I must apologize for the 'multi-level' nature) are given five sample tables from the Dictionary of π-electron calculations together with the print-outs of the data tapes used and the same data in manuscript form to show how forms have been devised to facilitate the writing of the data. The duplicated versions of these forms (of which I have the stencils) differ in a few minor respects only from those given here.

MERCURY AUTOCODE

Programmes for the Computation of Huckel M.O.'s and Derived Quantities. Notes for the User.

1. The Huckel Molecular Orbital Method.

For a description of the method and definition of terms and quantities used the user is referred to the introductory matter in the "Dictionary of π-electron calculations" by Coulson and Streitwieser, Pergamon Press 1964. The tables in this book were produced by the programmes now being described. It will be referred to below as DπEC.

2. Scope of the Programmes.

The Programmes are designed to produce the eigenvalues and eigenvectors (Energy levels and M.O. coefficients) from the Secular Matrix derived from any conjugated system of π-electrons in the approximation where overlap is neglected. From these they also calculate π-electron charges, π-bond orders, free valences and atom-atom, bond-bond and atom-bond polarizabilities. Facilities are available for use to be made of the symmetry of the molecule both to speed up the calculation and to reduce the size of tables printed.

3. The Different Versions available.

For different sorts of molecule different versions of the programme involving slightly different data layout are available; some of these are of more general applicability than others. The five chief versions are known by letters. They are:

S most general. Any number of heteroatom and hetero-bond (in this context a

hetero-bond is one whose resonance integral differs from β_o) parameters may be given. Also non-bonded interactions may be included. Use of symmetry is made in tabulation only, so this programme is slower than C or D for symmetrical molecules.

H for hydrocarbons, where all bond matrix elements are 1. Use may be made of symmetry to shorten tables but, in cases of degeneracy, orbitals belonging to the symmetry species will not necessarily be given.

E as H, but a single pair of hetero-parameters, one for atoms, one for bonds - must be given. It is possible to restart with other pairs of parameter values without re-reading the whole data.

C for molecules with C_{2v} or C_{2h} symmetry. By setting up matrices for the two symmetry species and solving them separately much time is saved. Hetero-atoms and bonds can be treated.

D for hydrocarbons with D_{2h} symmetry. Full use is made of symmetry to speed up the calculations. No hetero-atoms allowed.

The actual programmes differ only in the parts which read the data and calculate the eigenvalues and eigenvectors. They all incorporate Autocode Library Programme - 517 for the matrix diagonalisation and

have identical chapters for calculating, and printing the 'Derived Quantities'.

4. Choice of Programme for a particular problem.

Hydrocarbons - all bond matrix elements 1

if D_{2h} symmetry use D - could also use S or H or C

if C_{2v} or C_{2h} symmetry use C - Could also use S or H

if No symmetry use H - could also use S

if D_{3h} or D_{5h} symmetry use S - as full use of 3-fold or 5-fold symmetry to reduce size of tables cannot be made with C. C,however, is quicker if large tables are not wanted.

if D_{6h} symmetry use S - as full use of 6-fold symmetry (to reduce size of tables) cannot be made with D.

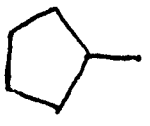
Heterosystems.

if only 2 parameters: h for one type of atom and k for one type of bond. Tables may be produced for several different pairs of values of h, k by using E. However in cases where degeneracy occurs S is to be preferred as orbitals belonging to symmetry species may be obtained if appropriate.

if there are more than 2 parameters or high symmetry, programmes C or S should be used.

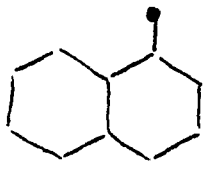
if non-bonded interactions, i.e. H_{rs} matrix elements where r is not a neighbour of s, are to be included then only S may be used.

Examples of optimum choice of programme.

Fulvene 

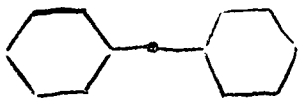
Hydrocarbon, C_{2v} symmetry C

1-Naphthyl-methyl



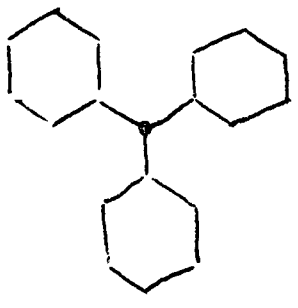
Hydrocarbon radical, no symmetry. H

Diphenyl-methyl



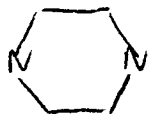
Hydrocarbon radical, D_{2h} symmetry D

Triphenyl-methyl



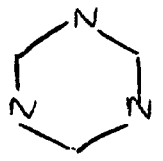
Hydrocarbon radical, D_{3h} symmetry. S
(consider as C_{2V})

Pyrazine



Heteromolecule: one sort of heteroatom, one sort of heterobond. E

s-Triazine



Heteromolecule: D_{3h} symmetry. S

Specimen data layouts and tables for some of the above molecules are given in Appendix I to these notes.

5. <u>How the calculated numbers are tabulated</u>.

For examples see DTEC and appendix I to these notes. (See also Section I.14 of this thesis).

The output will begin with titles of the Programme used. Next will come the heading from the data tape. After this will come as many of the following tables as are asked for by suitable settings of parameters in the Data.

Query Prints. If HS4 is not set on input a small column of query prints will head the tables. These may be of use in locating data or reader errors and details may be obtained from the author if required.

Orbital Energies. A column of eigenvalues to 7 places of decimals. These are numbered upwards from no.1 which is the most strongly bonding orbital. If so desired the unoccupied orbitals may be omitted. For hydrocarbons energies with inclusion of overlap (S =0.25) may also be given. For hetero-molecules these are usually suppressed as the simple formula for them is not applicable. Programmes C and D give a symmetry label opposite each energy level. This label is explained fully in DπEC. (See also Section I.9 of this thesis).

Total π-energy. This is computed assuming that 2 electrons go into each level until all electrons are accounted for.

M.O.Coefficients. Orbitals are tabulated vertically in horizontal sets of 6. Each column contains:

orbital number

energy (to 5 places of decimals)

symmetry label (if appropriate)

coefficients corresponding to atomic orbitals listed in the margin.

With Programmes S, H and E the atomic orbitals for which coefficients are quoted may be either

(i) all atomic orbitals

or (ii) those in a list specified in the data ('selected atoms')

With Programmes C and D a list of 'selected atoms' - i.e. those not related to others by symmetry - is generated by the programme from the data.

Charges and Bond-Orders. Two different tabulations of these are available.

(i) A matrix including all charges, bond-orders and non- bonded bond-orders (bond-order-like quantities) - broken into groups of 6 columns. The number of columns may be reduced to that of a list of atoms specified or generated (the 'selected atoms') if so required. If, however, a complete matrix is asked for only the lower triangle will appear.

(ii) Labelled columns of bond orders and charges for all bonds and atoms or for 'selected' bonds and atoms.

Free valences. These will appear in a single column below the charge-bond order Matrix or to the right of the bond orders and charges.

Polarizabilities. Two tabulations are available for each of the 3 sorts of Polarizability.

(i) As a matrix like the Charge-Bond Order Matrix described above

(ii) A single column of individual quantities for pairs of atoms/bonds given in the data. The column may be headed by all the self polarizabilities if desired (in the case of atom-atom and bond-bond).

6. Layout of the Datatapes.

(a) General Considerations about the Data tapes for the Programmes.

In general the data for any one molecule has four parts.

(i) A heading - confined to beginning and end of the tape.

(ii) Numbers describing the size and topology of the molecule and the values of certain matrix elements.

(iii) Numbers describing the symmetry of the molecule (if appropriate)

(iv) Parameters instructing the computer which quantities are to be calculated and tabulated.

Exact order of these different for different Programmes

The Heading.

The first instruction in the programme is HALT, and control returns to this point when calculation and tabulation for any one molecule is complete. The next set of instructions is a "heading reproduction sequence" which reads characters from the tape and if they are not erase characters reproduces them on the output tape up to but excluding the first 'n' or '?' (tape value 29). A heading of indefinite length may thus be put on the data tape provided only that it is suitably terminated. Blank tape included in the heading is useful for locating the beginning of a new set of tables in the output. Further headings at the end of the data tape will be reproduced on

clearing the final HALT, being treated as though they were the beginning of a new data tape. These headings should not be terminated unless no more data follows when they should be terminated "n → CR" so as to stop on the first READ instruction.

All other data is read in by the AUTOCODE Read instruction. In the description below numbers and parameters are referred to by the name of the Autocode Variable or Index into which they are read.

Data tapes for the 5 programmes.

Duplicated forms have been prepared to facilitate the preparation of data for the programmes. The following notes should be read in conjunction with the specimen forms provided in Appendix I.

Notes on preparation of the Data.

(b) Programme S

Data consists of: Heading - properly terminated by

'n' or '?'.

N. Number of atoms - max 60.

P. Number of bonds - max 80.

S. Number of Heteroatoms and/or Non-bonded

interactions - max 511.

G. Number of π electrons $\geq$N.

list of bonds

list of hetero-atoms and non-bonded interactions

Un Energy/coefficient parameter

Q and list)
) "Selected atoms and bonds"
J and list)

Vn Wn Xn Yn Zn Polarizability Parameters etc.

G. symmetry code No.

Symmetry data.

List of pairs of atoms/bonds for polarizabilities

(if wanted)

S: If there are no heteroatoms or non-bonded interactions and all bond matrix elements are 1; put S $\leq$ -1.

If bond matrix elements are not all 1 put S = 0 and give value of every such matrix element (including those that are 1) after the bond in the list below.

G: If S = -1, G is automatically put $\geq$N and should be omitted from the data.

N.B. G - N $\leq$ 2.

List of bonds: Number the molecule arbitrarily.

(Occasionally certain numberings will lead to matrices which are not correctly solved by Programme - 517; re-numbering will often get round this difficulty). List of the bonds in

strict dictionary order (see example) give the appropriate matrix element in units of β if and only if $S \geqslant 0$.

Heteroatoms and Non-bonded Interactions: All elements of the secular matrix other than those corresponding to bonds will be automatically set to zero unless set here. These must appear in strict dictionary order and must be in the form:

B	C	U
Atom No.	Atom No.	Matrix element

N.B. Only the upper triangle of the secular matrix is set up and used. Thus all bonds and non-bonds must be given with the lower atom number first.

U_n: see general note 2.

O, J: see general note 1.

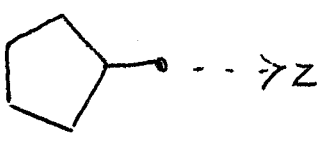
V_n, W_n, X_n, Y_n, Z_n see general note 3.

G: This code number should be set according to the symmetry of the molecule.

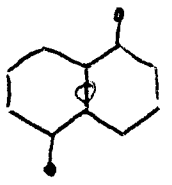
0: No symmetry.

1: Any symmetry but symmetrization of sets of degenerate orbitals is not to be carried out.

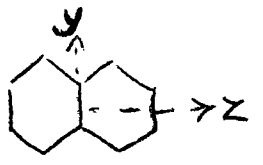
2. C_{2v} e.g.



3: C_{2h} e.g.

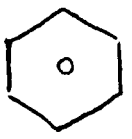


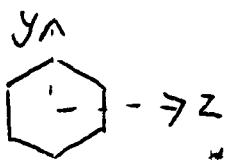
4. D_{2h} e.g.



5: D_{nh} as C_{2v} e.g.



6: D_{nh} as C_{2h} e.g. 

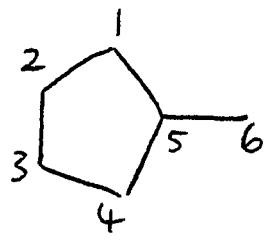
7: D_{nh} as D_{2h} e.g. 

According to the value of G there should follow certain symmetry data:

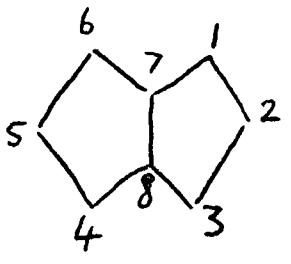
if G = 0 No more data.

if G = 1 Follow with H - value determined as G - indicating the symmetry to be assumed when looking for symmetry in the orbital coefficients. After H give 6 atom numbers which will be used by the programme to look for symmetries in the coefficients. These are defined thus: the first three numbers are completely independent of the second three. The first pair of each set should be related by the symmetry element if H = 2 or 3 or by the axis O_y if H = 4. The third atom of each set is a dummy (put =0, say) unless H = 4 when it should be related to the second by the axis O_z. If two such sets of atoms do not exist the only one should be repeated - as is done in the example in E (Appx.I), and in II below.

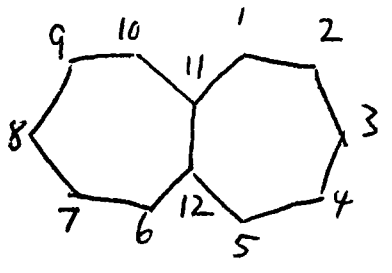
Examples: I



II



III



atom nos.: 2 3 0 1 4 0 | 1 6 4 1 6 4 | 1 10 6 2 9 7

If H = 0 six dummy atoms must be given.

If G $\geqslant$ 2 the symmetry data consists of a complete description of the relation of the various atoms to the symmetry elements. It is used in full only

when degenerate eigenvectors require to be symmetrized. If it is known that there are no degeneracies the G = 1 code may be used. If three asterisks are printed instead of a symmetry label in the output this means that no symmetry or anti-symmetry of the permissible type has been found - probably due to a data error; in these cases the list of selected atoms is automatically replaced by a complete list of atoms when the orbital is tabulated.

Nature of the complete description: Atoms are divided into types according as they lie on or off the symmetry elements - for each type the number of sets in such positions should be given followed by a list of these sets in the layout prescribed below.

G = 2 or 3 . Bn: Number of pairs related by the single symmetry element - (Theor.Max 60)

List of pairs. For G = 2, atoms on one side of Oz should consistently precede those on the other

Dn: Number of atoms on the symmetry element. Max 30.

List of atoms.

G = 4. An: Number of sets of 4 atoms in general positions (Not on Oz or Oy) List of sets; (each set to be numbered anti-clockwise from Oz).

Bn: Number of pairs of atoms on Oz

list of pairs (aton on +Oz axis first)

Cn: Number of pairs of atoms on Cy

list of pairs (atom on +Cy axis first)

Max (An + Bn + Cn) = 29

Dn: Atom at O (= 1 or 0)

list - (a single no.).

G> 4 Where the molecule has more symmetry than the symmetrization chapter can deal with, it will be necessary to quote MO coefficients for more atoms than the list of completely independent ones already given as 'selected atoms'. These extra selected atoms must be given here as a list of atom numbers preceded by the number of extra atoms (Q). This supplementary list will be used only for tabulating the MO coefficients.
(An example is given on the S form in Appx.I. Selected atoms are nos. 1 and 2 - extra atoms, nos. 3 and 4).

After this list give full symmetry data as if G were G - 3

(c) Programme H.

Data consists of :

Heading

N

P

list of bonds

Un

Q and list

J and list

Vn, Wn, Xn, Yn, Zn (actually read in as V, W, X, Y, Z)

G

6 atom nos. for comparison of coefficients

List of pairs of atoms/bonds for polarizabilities.

The 6 atom numbers for comparison of coefficients are to be chosen as described for the case G = 1 for

programme S except that if G $\leqslant$ 1.5 they are to be omitted altogether.

Other numbers and parameters should be constructed exactly as for S.

(d) Programme E

Data consists of: Heading

N, P, list of bonds } as for H

Heteroatoms: Number of + list
(give atom nos.) Max 5

Heterobonds: Number of + list
(number according to order in bond list) Max 24

initial values of parameters 'h' and 'k' for above.

Un
Q and list as for H
J and list
Vn, Wn, Xn, Yn, Zn (read in as V, W, X, Y, Z)
3 as for H
6 atoms

List of pairs of atoms/bonds for polarizabilities

Further pairs of values of 'h' and 'k'

Use of handswitch 5 with Programme E.

For this programme there may be only one Kind of heteroatom and one kind of heterobond. Further pairs of values for the parameters 'h' and 'k' for these may be read in if HS 5 is put up before clearing the HALT at the end of a calculation. All the other data are stored (except lists of pairs of atom/bonds for polarizabilities if these are being tabulated in

this form; such lists must thus be repeated in toto between each pair of parameter values and the next) and a complete recalculation is made with the new values. If Handswitch 5 is down a new heading will be read on clearing HALT.

The pair of parameters being used is printed out in the form

H 1.0000
K 1.5000

by the programme at the head of the appropriate set of tables.

(e) Programme C

This programme is confined in its application to molecules belonging to the point groups C_{2v} or C_{2h} or molecules which may be considered as having one of these two symmetries. Heteroatoms and bonds are allowed but no non-bonded interactions.

Data consists of: G 2 for C_{2v}, 3 for C_{2h}

Q Number of sets (related by symmetry) of heteroatoms

C (omit if Q = -1), number of π-electrons

Description of molecule according to symmetry.

Bonds between atoms of one set ('internal') } Total Max 13

Sets of Heteroatoms }

Bonds between atoms of two sets ('external') Max 47, 31 if heteros

Un, Vn, Wn, Xn, Yn, Zn.

The description of the molecule according to symmetry is exactly as described under G = 2, or 3 in the symmetry

data for Programme S.

In this Programme and Programme D sets of atoms related by symmetry are numbered from 0 starting with those in general positions and ending with those in the most special positions. 'Internal' bonds and sets of heteroatoms are referred to by a single no. - their ordinal no. just mentioned. 'External' bonds are described by a pair of such nos., the lower to come first; they are subdivided according to their relation to the symmetry elements - for details see the form. If $\underline{Q} \geqslant 0$ each bond must be followed by the appropriate matrix element in units of β, if $\underline{Q} \geqslant 1$ each set of heteroatoms by its coulomb term also in units of β.

(f) Programme D.

For molecules with D_{2h} symmetry only. No heteros allowed. Heteromolecules with this symmetry must be done by Programme E or S.

Data consists of: Description of molecule according to symmetry

Sets bonded internally	Max 12
Sets bonded externally	Max 40

Un, Vn, Wn, Xn, Yn, Zn.

The description of this molecule is as described under G = 4 in the symmetry data for programme S.

The method of description of bonds is best seen from the layout of the form. Note that the number of sets of bonds of each type must be given even if it is 0.

General Note 1.

Selected Atoms and Selected Bonds.

Use of the parameters Q and J in versions S, H and E. In these programmes no use is made of the symmetry to facilitate the calculations and so the computer must be told if and how the tables may be reduced in size because of molecular symmetry. The parameters Q and J and the lists which must follow each are used for this. These lists are referred to as listsof Selected Atoms/Bonds.

If quantities are to be quoted for all atoms and bonds Q should be put equal to N, and then J and both lists omitted.

A list of selected bonds consisting of all those whose first atom is a selected atom will be generated by the programme if Q is put equal to the number of selected atoms and followed by a list of Q atoms. Such a list, however, may not be adequate. In this case add 100 to Q and follow its list by J, the number of selected bonds, and a list of those bonds numbered according to their position in the bond list (which starts at 1).

If $Q < 100$, J and its list must be omitted.

If $Q \neq N$, $30 \geqslant Q$ and $45 \geqslant J$

Programmes C and D

Those atoms given as the first members of sets related by symmetry are used as selected atoms. A list of selected bonds is generated by the programme as it works out which atoms are bonded.

Note that if Selected Atoms and Bonds are given they will automatically be used to reduce the size of tables of orbital coefficients, charges and bond orders when listed separately, free valences and atom-atom and bond-bond self-polarizabilities. They will only be used to reduce the size of matrices (Charge-bond order or Polarizability) if the appropriate parameter is set to 200. (See general note 3)

General Note 2.

How to choose the value of Un - the energy/ coefficient parameter.

Wanted:	Nothing	Un 0
	Total π-energy only	0.5
	Coefficients only	1
	Energies only	2
	Energies and Coefficients	3

to this value of Un

add: 0.5 if all orbitals wanted (rather than just occupied).

0.1 if overlap-included values not wanted (and not using programme E or programme S with $S \geqslant 0$; in these latter cases 0.1 is added by the programme, so if overlap included values should nevertheless be wanted in these circumstances 0.1 should be subtracted from the Un which is to appear in the data).

General Note 3.

The Parameters Vn, Wn, Xn, Yn and Zn. How to choose their values.

If none of a particular quantity is required set the parameter at zero.

Vn Charge-bond order parameter.

Bond Orders for all bonds (or selected bonds if these have been given)	1
Bond Orders as above + charges for atoms (all or selected)	2
Lower triangle of symmetric complete matrix of charges and Bond Orders. Divided into blocks of 6 columns.	300
Matrix with N rows and Q columns, where Q is number of selected atoms. Divided into blocks of 6 columns.	200
Wn Free Valence Parameter. If wanted	1
Xn Atom-Atom / Yn Bond-Bond } Polarizabilities Parameter.	
Matrices as for charge-bond order matrix	300 / 200
Column of Self-Polarizabilities for list of Selected Atoms/Bonds	100
Polarizabilities for a list of pairs (max 92) of atoms/bonds given at the end of the data	Number of pairs
Column of Selfs + those from a list	100 +Number of pairs

Zn Atom-Bond Polarizabilities Parameter

Complete Rectangular matrix with N columns and P rows	300
Rectangular matrix with Q columns and P rows	200
List as for Xn,Yn	Number of pairs

In lists of pairs bonds should be numbered by their order in the bond list, for Zn atoms should precede bonds.

The lists for Xn,Yn,Zn should appear in that order at the end of the data. They are not read in until the calculation of these polarizabilities is about to take place.

7. Operating Instructions.

Autocode and Matrix in machine.

Programme in reader.

HS.4 up (to suppress queries if required) all other switches clear

ITB. Programme is read in (~5 min) ,HALTS.

Data in reader.

H.S.9 to clear 'HALT'

At end of each set of calculations programme will HALT.

To read new set of data: tap HS.9.

Programme E only:

To read in a pair of values of the parameters 'h' and 'k' for a repeat calculation. Set HS.5, before tapping HS.9 to clear HALT.

Note: Programmes C,D.H have been output in binary form and these binary versions may be used to save input time.

8. Availability of the programmes.

Copies of the programmes and further information about them may be obtained from the Author at the address below.

M.D.Poole,
The Mathematical
Institute,
10, Parks Road,
Oxford.

APPENDIX I TO APPENDIX A TO CHAPTER I

Sample tables from the dictionary of π-electron calculations.

A specimen calculation done with each version of the Programme is given in the following pages.

The print-out of the data tape and the manuscript data are given on facing pages, followed by the actual computer output as reproduced in the book.

The versions of the programmes used were identical in all major respects with those given in Appendix B to this chapter, but there have been some minor revisions which affect certain details of the output.

The calculations are:

Programme S	s-triazine	$h_N = 2.0$, $k_{CN} = 1.0$
Programme H	1-naphthyl-methyl	
Programme K	pyrazine-like systems	
Programme C	fulvene	
Programme D	diphenyl-methyl.	

A20

```
*※


H     2.000
K     1.000

n
6
6
3
6
1    2    1
1    6    1
2    3    1
3    4    1
4    5    1
5    6    1
1    1    2
3    3    2
5    5    2
3.5
102
1    2
1
1
200    1    200    0    0
5
2
3    4
2
6    2
5    3
2
1
4
```

DATA TAPE FOR HMO PROGRAMME - VERSION S

N	6	Number of atoms
P	6	Number of bonds
S	3	No. of heteros
G	6	No. of π-elecs (S+-1)

Bonds k_{rs} (S+-1)

1	1	2	1
2	1	6	1
3	2	3	1
4	3	4	1
5	4	5	1
6	5	6	1
7			
8			
9			
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44			
45			
46			
47			
48			
49			
50			

Heteroatoms:

1	1	1	2
2	3	3	2
3	5	5	2
4			
5			
6			
7			

Headings: - To be reproduced on output.

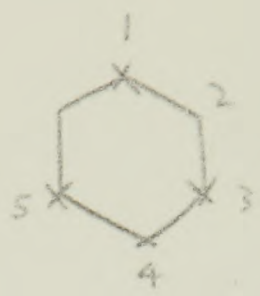
S-TRIAZINE

H 2.000

K 1.000

n

Numbered diagram of Molecule



Un	3.5	Energy and orbital coefficient parameter (General Note 2).
Ω	102	Number of 'selected atoms'.
List:-	1 2	
J	1	Number of 'selected bonds'
List:-	1	

see Gen note 1

Output parameters for derived quantities. (Gen note 3)

Vn	200	Wn	1	Xn	200	Yn	0	Zn	0

Symmetry description of the molecule.

G | 5 | Point Group Code Number

If G=4

An |

Bn |

Cn |

Dn |

If G=2or3

Bn | 2

6 2
5 3

Dn | 2

1
4

If G>4

Ω | 2

List of extra selected atoms.

3 4

then continue as if G were G-3

If G=1

H |

Atoms for comparison of coefficients:

1
2
3
4
5
6

H 2.000
K 1.000

ENERGY

	S=o
1	3.2360680
2	2.4142136
3	2.4142135
4	-0.4142135
5	-0.4142135
6	-1.2360679

TOTAL PI ENERGY
16.1289903

COEFFICIENTS

	1	2	3	4	5	6
E	3.23607	2.41421	2.41421	-0.41421	-0.41421	-1.23607
	B1-SZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
1	0.49112	-0.75434	0.00000	0.31246	0.00000	-0.30353
2	0.30353	-0.15623	0.27060	-0.37717	-0.65328	0.49112
3	0.49112	0.37717	0.65328	-0.15623	0.27060	-0.30353
4	0.30353	0.31246	0.00000	0.75434	0.00000	0.49112

CHARGE - BOND ORDER MATRIX

	1	2
1	1.62048	0.53384
2	0.53384	0.37952
3	-0.08663	0.53384
4	-0.17326	0.08663
5	-0.08663	-0.17326
6	0.53384	0.08663

FREE VALENCES

1	0.66436
2	0.66436

POLARIZABILITIES

ATOM-ATOM

	1	2
1	-0.18170	0.07802
2	0.07802	-0.18170
3	0.00211	0.07802
4	0.02144	0.00211
5	0.00211	0.02144
6	0.07802	0.00211

107
1-NAPHTHYL-METHYL

SYMM*ETRY. C1H

n
11
12
1 2
1 9
1 11
2 3
3 4
4 10
5 6
5 10
6 7
7 8
8 9
9 10
3
11
1 1 300 300 300
0

REFERENCES

31 126 131 144 145 153 161 185 191 *221 250 265 371
384 389 401 403

DATA TAPE FOR HMO PROGRAMME - VERSION H

Use only if Symmetrization of orbitals is not necessary or not wanted.
(No Heteroatoms)

N 11	Atoms
P 12	Bonds

Bonds

1	1	2
2	1	9
3	1	11
4	2	3
5	3	4
6	4	10
7	5	6
8	5	10
9	6	7
10	7	8
11	8	9
12	9	10
13		
14		
15		
16		
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60		

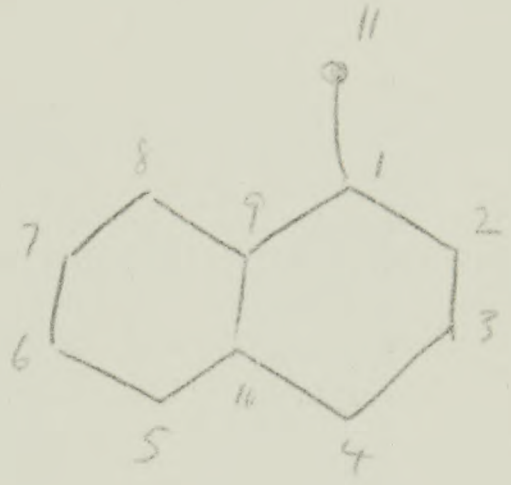
Headings: - To be reproduced on output.

107

1-NAPHTHYL METHYL

SYMMETRY C1H

Numbered diagram of Molecule



Un	3	Energy and orbital coefficient parameter (General Note 2)
Q	11	Number of selected atoms
List:-		
J	—	If bonds not to be selected automatically add 100 to Q and put J = No. of selected bonds.
List:-		

see Gen note 1

Output parameters for bond orders, free valences, atom-atom, bond-bond and atom-bond polarizabilities respectively. (General note 3)

Vn		Wn		Xn	3π	Yn	3σ	Zn	3σ	
	1		1							

G	0	Point Group Code Number

Two sets of atoms related by the symmetry elements: -

107.
1-NAPHTHYL-METHYL

SYMMETRY. C1H

ENERGY

	S=0	S=0.25
1	2.3513652	1.4808565
2	1.6830185	1.1845948
3	1.4142136	1.0448155
4	1.0000001	0.8000001
5	0.7990816	0.6660287
6	0.0000000	0.0000000

TOTAL PI ENERGY

14.4953580	10.3525913

COEFFICIENTS

	1	2	3	4	5	6
E	2.35137	1.68302	1.41421	1.00000	0.79908	0.00000
1	0.37349	-0.38687	0.35355	0.00000	0.29298	0.00000
2	0.25579	-0.40752	-0.00000	0.40825	0.04281	-0.44721
3	0.22798	-0.29899	-0.35355	0.40825	-0.25878	-0.00000
4	0.28026	-0.09569	-0.50000	-0.00000	-0.24959	0.44721
5	0.26966	0.34158	-0.25000	0.00000	0.47234	-0.22361
6	0.20305	0.43693	0.00000	0.40825	0.31811	0.00000
7	0.20778	0.39379	0.25000	0.40825	-0.21815	0.22361
8	0.28552	0.22582	0.35355	0.00000	-0.49243	-0.00000
9	0.46357	-0.01373	0.25000	-0.40825	-0.17534	-0.22361
10	0.43103	0.13795	-0.35355	-0.40825	0.05933	-0.00000
11	0.15884	-0.22987	0.25000	-0.00000	0.36665	0.67082

BOND ORDERS

1	2	0.53147
1	9	0.43093
1	11	0.68813
2	3	0.67150
3	4	0.66774
4	10	0.53914
5	6	0.70851
5	10	0.55953
6	7	0.62305
7	8	0.68813
8	9	0.60798
9	10	0.53159

FREE VALENCES

1	0.08153
2	0.52909
3	0.39282
4	0.52517
5	0.46401
6	0.40049
7	0.42088
8	0.43595
9	0.16155
10	0.10179
11	1.04393

POLARIZABILITIES

ATOM-ATOM

	1	2	3	4	5	6
1	-0.32107					
2	0.07698	-0.46110				
3	-0.00772	0.16004	-0.39470			
4	0.03856	0.02351	0.15747	-0.45793		
5	0.00546	0.00770	0.02193	-0.02273	-0.45633	
6	-0.00234	0.01390	-0.00010	0.01512	0.19490	-0.40068
7	0.00869	0.02298	0.02058	0.00387	-0.01988	0.12364
8	-0.01095	0.00473	-0.00332	0.00227	0.10928	-0.01431
9	0.03886	0.02670	0.03074	0.00745	0.00682	0.06442
10	-0.00199	0.03982	-0.00824	0.08017	0.09207	-0.00684
11	0.17552	0.08474	0.02332	0.15224	0.06078	0.01229

	7.	8	9	10	11
7.	-0.42091				
8	0.17552	-0.42397.			
9	-0.00975	0.12369	-0.36618		
10	0.05249	-0.00427.	0.08314	-0.32845	
11	0.04278	0.04132	-0.00588	0.00210	-0.58921

BOND-BOND

	1- 2	1- 9	1-11	2- 3	3- 4	4-10
1- 2	-0.32907.					
1- 9	0.05869	-0.30477.				
1-11	0.22917.	0.15390	-0.33709			
2- 3	0.17142	-0.04217.	-0.07522	-0.30297.		
3- 4	-0.10287.	0.02029	0.05978	0.26904	-0.30435	
4-10	0.02991	-0.05858	0.01734	-0.10418	0.17407	-0.33036
5- 6	-0.00034	-0.01660	0.01566	-0.01822	0.01975	-0.05170
5-10	-0.00877.	0.01292	-0.00473	0.04204	-0.05679	0.15494
6- 7.	-0.00518	0.03068	-0.02033	0.01718	-0.01836	0.03961
7- 8	-0.00388	-0.04588	0.03772	-0.00247.	-0.00515	0.00071
8- 9	-0.00637.	0.11427.	-0.05961	0.00747.	0.00524	-0.00252
9-10	-0.03271	0.07725	-0.01658	0.03807	-0.06065	0.13077.

	5- 6	5-10	6- 7.	7- 8	8- 9	9-10
5- 6	-0.23324					
5-10	0.17957.	-0.28992				
6- 7.	0.22217.	-0.11147.	-0.29029			
7- 8	-0.12593	0.06540	0.20751	-0.25162		
8- 9	0.08206	-0.08920	-0.11892	0.20901	-0.27512	
9-10	-0.07317.	0.10600	0.04740	-0.08542	0.13369	-0.26466

ATOM-BOND

	1	2	3	4	5	6
1- 2	0.00000	-0.12000	-0.00000	-0.12000	-0.03000	0.00000
1- 9	0.00000	-0.06000	0.00000	-0.06000	-0.01500	-0.00000
1-11	-0.00000	0.18000	0.00000	0.18000	0.04500	0.00000
2- 3	-0.00000	-0.20000	0.00000	0.20000	0.05000	-0.00000
3- 4	0.00000	0.20000	-0.00000	-0.20000	-0.05000	0.00000
4-10	-0.00000	-0.12000	-0.00000	-0.12000	0.07000	-0.00000
5- 6	0.00000	-0.04000	0.00000	-0.04000	-0.06000	0.00000
5-10	0.00000	0.06000	0.00000	0.06000	-0.03500	0.00000
6- 7.	-0.00000	0.04000	-0.00000	0.04000	0.06000	0.00000
7- 8	-0.00000	-0.02000	0.00000	-0.02000	-0.05500	0.00000
8- 9	0.00000	0.02000	-0.00000	0.02000	0.05500	-0.00000
9-10	0.00000	0.06000	0.00000	0.06000	-0.03500	-0.00000

	7.	8	9	10	11
1- 2	-0.03000	0.00000	-0.03000	-0.00000	0.33000
1- 9	-0.01500	0.00000	-0.01500	0.00000	0.16500
1-11	0.04500	0.00000	0.04500	0.00000	-0.49500
2- 3	0.05000	-0.00000	0.05000	0.00000	-0.15000
3- 4	-0.05000	-0.00000	-0.05000	-0.00000	0.15000
4-10	0.07000	0.00000	0.07000	0.00000	0.03000
5- 6	0.04000	0.00000	0.04000	0.00000	0.06000
5-10	-0.03500	0.00000	-0.03500	-0.00000	-0.01500
6- 7.	-0.04000	0.00000	-0.04000	-0.00000	-0.06000
7- 8	-0.05500	-0.00000	0.04500	-0.00000	0.10500
8- 9	0.05500	-0.00000	-0.04500	0.00000	-0.10500
9-10	-0.03500	0.00000	-0.03500	0.00000	-0.01500

REFERENCES

31 126 131 144 145 153 161 185 191 221 250 265 371
384 389 401 403

A27

132
PYRAZINE-LIKE SYSTEMS*

SYMMETRY. D_{2H}

6 PI ELECTRONS

```
n
6
6
1   2
1   6
2   3
3   4
4   5
5   6
2   1   4
1   1
0.5   1
3.5
1 0 2
1   2
2
1   2
200   1   200   200   200
6
4
2   6   5   2   6   5

1   1
2   1
```

REFERENCES

1 14 79 87 130 188 203 225 233 236 248 271 291***
303 298 284 400

DATA TAPE FOR HMO PROGRAMS - VERSION 4

Heteromolecules: 1 atom parameter, 1 bond parameter.

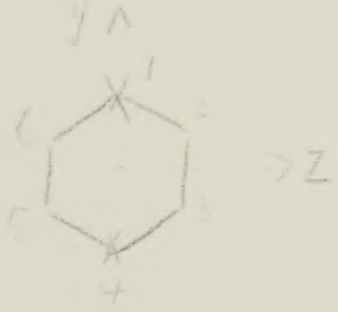
N 6	Atoms
P 6	Bonds

Bonds

1 1 5
2 1 2
3 2 3
4 3 4
5 4 5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
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57
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59
60

Headings: - To be reproduced on output.

Numbered diagram of Molecule



HETERO3; - Atoms 2 List: 1 7

Bonds 1 List: 1

Initial values of the parameters 'h' and 'k':

h 0.5 k 1

Un 1.5 Energy and orbital coefficient parameter (General note 2)

Ω 102 Number of selected atoms — see Gen note 1

List:- 1 2

J 2 If bonds not to be selected automatically add 100 to Ω and put J = No. of selected bonds

List:- 1 3

Output parameters for bond orders, free valences, atom-atom, bond-bond and atom-bond polarisabilities respectively. (General note 3)

Vn	Wn	Xn	Yn	Zn
2.0	1	2.0	2.0	2.0

Mn 6 Number of π-electrons

SYMMETRY: 6 4 Point Group Code Number

Two sets of atoms related by the symmetry elements.

2 6 5 2 6 5

Further pairs of values of the parameters 'h' and 'k'.

h	k
1	1
7	1

132
PYRAZINE-LIKE SYSTEMS

SYMMETRY. D2H

6 PI ELECTRONS

H 0.5000
K 1.0000

ENERGY

	S=0
1	2.1861407
2	1.3507811
3	1.0000000
4	-0.6861406
5	-0.9999999
6	-1.8507810

TOTAL PI ENERGY
9.0738437.

COEFFICIENTS

	1	2	3	4	5	6
E	2.18614	1.35078	1.00000	-0.68614	-1.00000	-1.85078
	B3U-SYSZ	B1G-SYAZ	B2G-AYSZ	B3U-SYSZ	A1U-AYAZ	B1G-SYAZ
1	0.45440	-0.60591	0.00000	0.54177	0.00000	-0.36451
2	0.38309	-0.25775	-0.50000	-0.32131	-0.50000	0.42845

CHARGE - BOND ORDER MATRIX

	1	2
1	1.14722	0.66050
2	0.66050	0.92639
3	0.03581	0.66065
4	-0.32130	0.03581
5	0.03581	-0.33935
6	0.66050	-0.07361

FREE VALENCES

1	0.41105
2	0.41090

POLARIZABILITIES

ATOM-ATOM

	1	2
1	-0.38414	0.15300
2	0.15300	-0.40144
3	-0.00765	0.14979
4	0.09345	-0.00765
5	-0.00765	0.10786
6	0.15300	-0.00156

BOND-BOND

	1- 2	2- 3
1- 2	-0.24509	0.20308
1- 6	0.19658	-0.13627.
2- 3	0.20308	-0.25165
3- 4	-0.12472	0.20308
4- 5	0.09412	-0.13627.
5- 6	-0.13627.	0.10631

ATOM-BOND

	1	2
1- 2	0.06913	0.00674
1- 6	0.06913	-0.06716
2- 3	0.02346	-0.07766
3- 4	-0.01991	0.04226
4- 5	-0.01991	-0.03106
5- 6	0.02346	0.05421

H 1.0000
K 1.0000

ENERGY

	S=0
1	2.4142136
2	1.7320508
3	1.0000000
4	-0.4142135
5	-0.9999999
6	-1.7320508

TOTAL PI ENERGY
10.2925290

COEFFICIENTS

	1	2	3	4	5	6
E	2.41421	1.73205	1.00000	-0.41421	-1.00000	-1.73205
	B_3U-SYSZ	B1G-SYAZ	B_2G-AYSZ	B_3U-SYSZ	A1U-AYAZ	B1G-SYAZ
1	0.50000	-0.62796	0.00000	0.50000	0.00000	0.32506
2	0.35355	-0.22985	-0.50000	-0.35355	-0.50000	-0.44404

CHARGE - BOND ORDER MATRIX

	1	2
1	1.28868	0.64223
2	0.64223	0.85566
3	0.06488	0.64434
4	-0.28868	0.06488
5	0.06488	-0.35566
6	0.64223	-0.14434

FREE VALENCES

1	0.44759
2	0.44548

POLARIZABILITIES

ATOM-ATOM

	1	2
1	-0.34572	0.14042
2	0.14042	-0.41172
3	-0.00392	0.12801
4	0.07271	-0.00392
5	-0.00392	0.12590
6	0.14042	0.02130

BOND-BOND

	1- 2	2- 3
1- 2	-0.25678	0.20189
1- 6	0.17623	-0.15377
2- 3	0.20189	-0.28370
3- 4	-0.11244	0.20189
4- 5	0.09677	-0.15377
5- 6	-0.15377	0.14720

ATOM-BOND

	1	2
1- 2	0.12757	0.01673
1- 6	0.12757	-0.12972
2- 3	0.04028	-0.15824
3- 4	-0.03135	0.07950
4- 5	-0.03135	-0.06273
5- 6	0.04028	0.11796

H 2.0000
K 1.0000

ENERGY

	S=0
1	3.0000000
2	2.5615528
3	1.0000001
4	0.0000000
5	-0.9999999
6	-1.5615528

TOTAL PI ENERGY
13.1231060

COEFFICIENTS

	1	2	3	4	5	6
E	3.00000	2.56155	1.00000	0.00000	-1.00000	-1.56155
	B_3U-SYSZ	B_1G-SYAZ	B_2G-AYSZ	B_3U-SYSZ	A_1U-AYAZ	B_1G-SYAZ
1	0.57735	-0.65719	0.00000	-0.40825	0.00000	0.26096
2	0.28868	-0.18452	-0.50000	0.40825	-0.50000	-0.46471

CHARGE - BOND ORDER MATRIX

	1	2
1	1.53047	0.57587
2	0.57587	0.73476
3	0.09080	0.59857
4	-0.19714	0.09080
5	0.09080	-0.40143
6	0.57587	-0.26524

FREE VALENCES

1	0.58031
2	0.55761

POLARIZABILITIES
ATOM-ATOM

	1	2
1	-0.23492	0.10059
2	0.10059	-0.45666
3	0.00202	0.05290
4	0.02970	0.00202
5	0.00202	0.19508
6	0.10059	0.10607

BOND-BOND

	1- 2	2- 3
1- 2	-0.28568	0.20360
1- 6	0.11217	-0.19783
2- 3	0.20360	-0.40376
3- 4	-0.08497	0.20360
4- 5	0.09305	-0.19783
5- 6	-0.19783	0.30115

ATOM-BOND

	1	2
1- 2	0.18618	0.05297
1- 6	0.18618	-0.22361
2- 3	0.04554	-0.33698
3- 4	-0.02650	0.13242
4- 5	-0.02650	-0.12146
5- 6	0.04554	0.29144

REFERENCES

24 14 79 87 130 188 203 225 232 236 248 274 291
293 298 384 400

A32

75
FULVENE

SYMMETRY. C2V

n
2
-1
2
1 4
2 2
2
5
6
1 1
1 0 1
1 2 2
1 0 2
3.5 200 1 200 200 200

ATOMIC LOCALIZATION ENERGIES

	L+	L-
1	2.0018	2.0018
2	2.2297	2.2297
6	2.2298	0.9938

REFERENCES

3 13 34 68 81 106 131 170 178 183 186 191 200
228 254 313 316 331 333 344 366 379 382 384 387 389
403 405

DATA TAPE FOR HMO PROGRAMME - VERSION C

G	2	2=C2V, 3=C2H
Q	-1	No. of sets of Heteroatoms
C	-	No. of π-electrons (Q=-1)

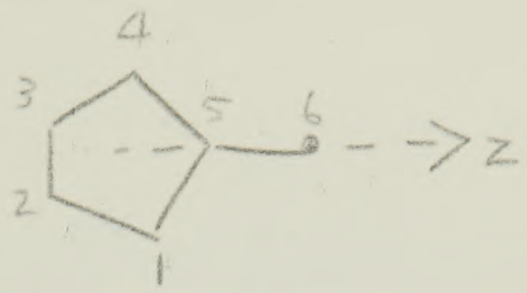
Headings:- To be reproduced on output.

75
FULVENE
SYMMETRY C2V
π

ATOM LIST

List	U	V
2	General pairs	
0	1	4
1	2	3
2		
3		
4		
5		
6		
7		
8		
9		
10		
11		
12		
13		
14		
15		
16		
17		
18		
19		
20		
21		
22		
23		
24		
25		
26		
27		
28		
29		

Numbered diagram of Molecule



BOND LIST

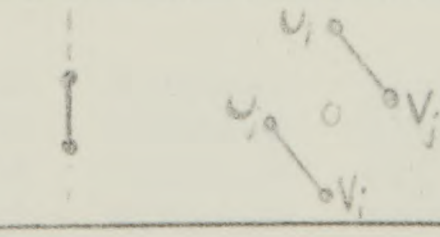
A. Pairs bonded internally. Give number of pairs followed by list according to their number in the atom list. If Q ≥0 follow each with the appropriate k_{rs}.

1 1

If Q ≥1 give here a list of Q sets of heteroatoms (numbered as atom list) each with appropriate h_r.

—

B. Pairs bonded externally.
Give number of each type then list of pairs of Nos. from the atom list and, if Q ≥0, the appropriate k_{rs}.

Bo		1	0 1
B1		1	2 3
B2		1	0 2

2	Atoms on the symmetry element
2	5
3	6

number in sequence with general pairs.

Output parameters for: Energy/Coefficients, Charges/Bond orders, Free Valences, Atom-Atom, Bond-Bond and Atom-Bond Polarizabilities. (Notes 2,3)

Un 2.5	Vn 200	Wn 1	Xn 200	Yn 200	Zn 200

75
FULVENE

SYMMETRY. C2V

ENERGY

	S=0	S=0.25	
1	2.1149075	1.3834436	B1-SZ
2	0.9999999	0.8000000	B1-SZ
3	0.6180340	0.5353222	A2-AZ
4	-0.2541017	-0.2713386	B1-SZ
5	-1.6180340	-2.7171404	A2-AZ
6	-1.8608059	-3.4794520	B1-SZ

TOTAL PI ENERGY

S=0	S=0.25
7.4658828	5.4375315

COEFFICIENTS

	1	2	3	4	5	6
E	2.1149	1.00000	0.6180	-0.2541	-1.6180	-1.8608
	B1-SZ	B1-SZ	A2-AZ	B1-SZ	A2-AZ	B1-SZ
1	0.42937	0.00000	0.60150	-0.35054	-0.37175	-0.43904
2	0.38512	0.50000	0.37175	0.27952	0.60150	0.15347
5	0.52297	-0.50000	0.00000	-0.19044	0.00000	0.66350
6	0.24728	-0.50000	0.00000	0.74948	0.00000	-0.35657

CHARGE - BOND ORDER MATRIX

	1	2	5	6
1	1.09233	0.77794	0.44910	0.21235
2	0.77794	1.07303	-0.09719	-0.30954
3	-0.11649	0.52024	-0.09719	-0.30954
4	-0.35488	-0.11649	0.44910	0.21235
5	0.44910	-0.09719	1.04699	0.75863
6	0.21235	-0.30954	0.75863	0.62229

FREE VALENCES

1	0.50502
2	0.43387
5	0.07522
6	0.97342

POLARIZABILITIES

ATOM-ATOM

	1	2	5	6
1	-0.50719	0.29243	0.04050	0.03038
2	0.29243	-0.43353	-0.00938	0.11947
3	-0.03641	0.06742	-0.00938	0.11947
4	0.18030	-0.03641	0.04050	0.03038
5	0.04050	-0.00938	-0.32069	0.25846
6	0.03038	0.11947	0.25846	-0.55816

BOND-BOND

	1- 2	1- 5	2- 3	5- 6
1- 2	-0.17377	0.15334	0.19998	-0.09848
1- 5	0.15334	-0.34879	-0.05679	0.17948
2- 3	0.19998	-0.05679	-0.36611	0.07971
4- 3	-0.09212	0.01105	0.19998	-0.09848
4- 5	0.01105	0.06170	-0.05679	0.17948
5- 6	-0.09848	0.17948	0.07971	-0.24172

ATOM-BOND

	1	2	5	6
1- 2	0.09211	0.06644	-0.01509	-0.15923
1- 5	-0.03084	-0.07609	-0.01529	0.24263
2- 3	-0.10175	-0.00834	-0.01877	0.23895
4- 3	0.04002	-0.02425	-0.01509	-0.15923
4- 5	-0.08293	-0.03748	-0.01529	0.24263
5- 6	0.08339	0.07971	0.07952	-0.40573

ATOM LOCALIZATION ENERGIES

	L+	L-
1	2.0018	2.0018
2	2.2397	2.2397
6	2.2298	0.9938

REFERENCES

3 13 34 68 81 106 131 170 178 183 186 191 200
228 254 313 316 331 333 344 366 379 382 384 387 389
403 405

113
DIPHENYL-METHYL (CODE NO. 13.2.6.134)

SYMMETRY. D_{2H}

```
n
2
2   8   12   6
3   9   11   5
2
1   7
4   10
0
1
13
0
0
0
0
0
1   0   1
0
0
2   0   2
    1   3
0
1   2   4
0
0
3   200   1   200   0   0
```

*REFERENCES

131 132 185 223 260 269 296 324 382 383 384 386 389
401 403

DATA TAPE FOR HMO PROGRAMS - VERSION D

A37

Headings:- To be reproduced on output.

113
DIPHENYL-METHYL
SYMMETRY D2H

N

ATOM LIST

2 General sets

V : U
- - - -
D : G

List

	U	V	D	G
0	2	8	12	6
1	3	9	11	5
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				

2 Pairs on z-axis

2	1	7	Number in sequence with general sets
3	4	10	V - - - U

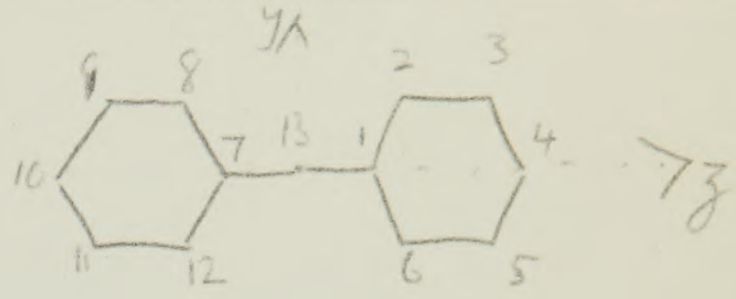
0 Pairs on y-axis

			U
			- - -
			V

1 Atom at the origin

4	13

Numbered diagram of Molecule



BOND LIST

A. Sets bonded internally. For each type give number of sets of that type, followed if non-zero by a list of sets of atoms numbered according to their position in the atom list. (the lower number always to come first)



Ao 0

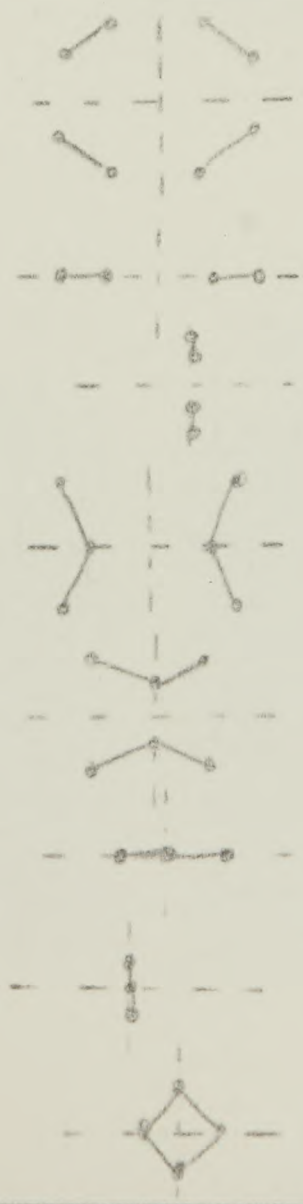
A1 0

A2 0

A3 0

A4 0

B. Sets bonded externally. As above but each set of bonds is described by a pair of numbers from the atom list - lower number first.



Bo 1 0 1

B1 0

B2 0

B3 2 0 2 / 1 3

B4 0

B5 1 2 4

B6 0

B7 0

Output parameters for: Energy/Coeffs., Charges/Bond orders, Free Valences, Atom-Atom, Bond-Bond and Atom-Bond Polarisabilities. (General Notes 2,3)

Un	Vn	Wn	Xn	Yn	Zn
3	200	1	200	0	0

II3
DIPHENYL-METHYL (CODE NO. I3.2.6.I34)

SYMMETRY. D2H

ENERGY

	S=0	S=0.25	
I	2.2360679	I.4342807.	B3U-SYSZ
2	I.9999999	I.3333333	B2G-AYSZ
3	I.4I42I35	I.0448I55	B3U-SYSZ
4	I.0000000	0.8000000	BIG-SYAZ
5	I.0000000	0.8000000	AIU-AYAZ
6	0.9999999	0.8000000	B2G-AYSZ
7.	-0.0000000	-0.0000000	B3U-SYSZ

TOTAL PI ENERGY

I7.3005625	I2.4248587.

COEFFICIENTS

	I	2	3	4	5	6
E	2.23607.	2.00000	I.4I42I	I.00000	I.00000	I.00000
	B3U-SYSZ	B2G-AYSZ	B3U-SYSZ	BIG-SYAZ	AIU-AYAZ	B2G-AYSZ
I	0.40825	0.28868	0.28868	0.00000	0.00000	-0.40825
2	0.27386	0.28868	0.00000	0.35355	0.35355	-0.204I2
3	0.204I2	0.28868	-0.28868	0.35355	0.35355	0.204I2
4	0.I8257.	0.28868	-0.40825	0.00000	0.00000	0.40825
I3	0.36515	0.00000	0.40825	0.00000	0.00000	0.00000

	7.
E	-0.00000
	B3U-SYSZ
I	0.00000
2	-0.3I623
3	0.00000
4	0.3I623
I3	0.63246

CHARGE - BOND ORDER MATRIX

	I	2	3	4	I3
I	I.00000	0.55694	0.00000	-0.25330	0.53384
2	0.55694	I.00000	0.69514	-0.00000	-0.00000
3	0.00000	0.69514	I.00000	0.64357.	-0.08663
4	-0.25330	-0.00000	0.64357.	I.00000	-0.00000
5	0.00000	-0.30486	0.00000	0.64357.	-0.08663
6	0.55694	-0.00000	-0.30486	-0.00000	-0.00000
7.	-0.00000	-0.I0973	0.00000	0.08004	0.53384
8	-0.I0973	0.00000	0.02847.	-0.00000	-0.00000
9	0.00000	0.02847.	-0.00000	-0.02310	-0.08663
I0	0.08004	-0.00000	-0.02310	0.00000	-0.00000
II	0.00000	0.02847.	-0.00000	-0.02310	-0.08663
I2	-0.I0973	0.00000	0.02847.	-0.00000	-0.00000
I3	0.53384	-0.00000	-0.08663	-0.00000	I.00000

FREE VALENCES

I	0.08433
2	0.47997.
3	0.39334
4	0.44491
I3	0.66436

POLARIZABILITIES

ATOM-ATOM

	1	2	3	4	13
1	-0.32184	0.09116	-0.00581	0.05392	0.07802
2	0.09116	-0.45956	0.18043	-0.00984	0.02683
3	-0.00581	0.18043	-0.39430	0.13896	0.00536
4	0.05392	-0.00984	0.13896	-0.43200	0.05152
5	-0.00581	0.08355	-0.01028	0.13896	0.00536
6	0.09116	0.02759	0.08355	-0.00984	0.02683
7	-0.00745	0.00990	-0.00044	0.00773	0.07802
8	0.00990	0.01474	0.00091	0.01863	0.02683
9	-0.00044	0.00091	-0.00003	0.00076	0.00536
10	0.00773	0.01863	0.00076	0.02181	0.05152
11	-0.00044	0.00091	-0.00003	0.00076	0.00536
12	0.00990	0.01474	0.00091	0.01863	0.02683
13	0.07802	0.02683	0.00536	0.05152	-0.38785

REFERENCES

131 132 185 223 260 269 296 324 382 383 384 386 389
401 403

APPENDIX B TO CHAPTER I

The following pages are teleprinter print-outs of the HMO Programmes described in chapter I. They should be read in conjunction with the flow charts in the chapter and the Block Diagram given in section I.11. All blocks in the last-mentioned diagram except the library version of Programme -517 are represented by programmes in this appendix, and the diagram should be used to see how the separate chapters of the programmes may be fitted together to give the five complete versions. Punched tapes for these programmes are held by the secretary at the Mathematical Institute, 10 Parks Road, Oxford.

The various chapters are given in this appendix in the following order: (S0 represents version 3, chapter 0, etc.)

S0, S1, M0, E0, HM1, C0, C1, D0, D1, HM2, C2, D2, 3, 4, 5,

Programme -51/ (autocode version with orthonormalization).

The print-outs are annotated at the left with arrows indicating the action of JUMP instructions and joining the two ends of REPEAT cycles. Notes are also given opposite instructions and groups of instructions to help in elucidating the action of the programmes. These notes are not intended to be a full explanation of all steps of the calculation, but should enable a reader familiar with the programming language to find his way around the programmes when used in conjunction with the flow charts and verbal descriptions given in chapter I of this thesis.

```
Programme 8
TITLE
SPARSE MATRIX - ELEMENTS UNITY OR READ FROM TAPE - POOLE - MI24

CHAPTERo                    see FLOW CHART 3
B→79
C→79
A→139
E→59
U→29
D→14
G→14
H→29
V→29

10)HALT
11)600(I)                   reproduce heading from data tape up to but
JUMP11,I≥31                 excluding first character with tape value 29.
JUMP12,I=29
630(I)
JUMP11

12)Gn=1
En=o                        constants throughout the programme
Ev3
Bnv4030
READ(N)                     constant for this chapter only
                            datum for auxiliary storage locations
£=N                         N = number of atoms
READ(P)
READ(S)                     P = number of bonds
                            S = number of non-bond matrix elements
GvE
JUMP2,S=-1
READ(G)
2)AnvEn
L=o(1)279
AL=En
REPEAT
Q=P-1
J=o(1)Q
READ(BJ)                    bond list
READ(CJ)
JUMP9,-1≥S
READ(UJ)                    k_rs for bond
9)REPEAT
J=o
JUMP17,-1≥S
W=o.1
K=280
JUMP14
17)K=280
W=En
14)B=K
O=o
I=o
Y=Gn
Q=N-1
```

```
L=o(1)Q
15)JUMP22,En≥Y
   JUMP13,O≥S
   READ(R)
   READ(T)
   O=O+1
   R=R-1
   T=T-1
22)JUMP23,L>R
   JUMP23,T=L
   Y=En
13)Z=En
   C=L
   D=C
   JUMP1
23)Y=Gn
   Z=Gn
   C=R
   D=T
1)Av£C+D-An
   JUMP5,A≥B
   M=XINTPT(A)
   JUMP16,En≥Z
   READ(AM)
   JUMP15
16)I=I+1
   AM=AM+E
   JUMP3,Q≠L
   K=M+1
5)JUMP6,J≥P
   Av£BJ-£+CJ-Gn-An
   JUMP6,A≥B
   ?M=XINTPT(A)
   JUMP18,-1≥S
   AM=UJ
   JUMP19
18)AM=Gn
19)J=J+1
   JUMP5
6)X7(An)Ao,K
   JUMP3,I≥N
   ?AnvB+An
   M=K-1
   M=M(-1)o
   AM=En
   REPEAT
   JUMP1
3)REPEAT

   READ(Un)
   UnvW+Un
   READ(O)
   DvBn
   JUMP23,O=N
   JUMP20,100≥O
   O=O-100
   X=Gn
   JUMP21
20)X=En
21)O=O-1
   I=o(1)O
   READ(HI)
   REPEAT
   JUMP22,En≥X
   READ(J)
   I=1(1)J
   READ(E(I-1))
   REPEAT
   JUMP21
22)T=P-1
```

set up the upper triangle of the complete secular matrix (in blocks of K elements if too big to be done in one go) in Ao ... from the list of bonds Bo-Co ..., reading and inserting non-bond matrix elements and adding the 'zero' 3 to each diagonal element.

Use of indices:

I	counter for diagonal 'zero' elements
J	counter for bonds
K	number of elements in a block
L	No. of row being set up
M	position of element being set up
N	order of the matrix
Q	counter for non-bond elements
P	number of bonds
Q	= N-1
R	row No. for non-bonds
T	col No.
S	number of non-bonds.

Meaning of Y and Z:

Y = 0 if position of a non-bond element has been read, but not its value.
= 1 otherwise
Z = 0 when the 'zero' diagonal element is being set up
= 1 otherwise.

output parameter for energy and coefficients

number of selected atoms

if O = N no list of selected atoms is defined
if O < 100 list of selected bonds must be generated

selected atoms

number of selected bonds
selected bonds.

```
      I=o
      J=o
   ┌──Q=o(I)T
   │  M=o
   │ →94)JUMP95,BQ≠HI          search bond list for those
   │  EJvQ+I                   whose first atom is in list
   │  J=J+I                    of selected atoms. Such bonds
   │ ┌JUMP96,45≥J              taken as selected bonds in Bo ...
   │ │ JUMP9I
   │ →95)M=M+I
   │  JUMP96,M>O
   │  I=I+I
   │ ┌JUMP94,O≥I
   │ │ I=o
   │ └JUMP94
   └→96)REPEAT
  ┌──→9I)O=O+I
  │    HnvJ
  │    HvBn-Hn
  │    DvH-£+Gn
  │    x7(D)Ho,O               store selected atoms
  │    x7(H)Eo,J               store selected bonds
  │ ┌──JUMP4
  └→│ 93)HnvP
    └→4)FnvO
      ┌I=489(I)493
      │READ(BI)
      └REPEAT
      Wnv N
      W=xFRPT(Un)              Read Vn,Wn,Xn,Yn,Zn - output parameters for
      ┌JUMP97,W≥o.1                                  derived quantities
      │Wnvo.5G                 if W < 0.5 antibonding orbitals need not be computed
      └→97)?W=Xn+Yn+Zn+W

      O=P
      AnvEn                    auxiliary store address for secular matrix
      Cnv£+Bn                  auxiliary store address for eigenvectors
      FvCn                                  (for Programme -517)
      x7(££+F)Hn,7             preserve output parameters etc.
      HnvG

      XnvBn
      YnvD-P
      ZnvYn-P
      x7(Yn)Bo,P
      x7(Zn)Co,P               store bond list
   ┌──JUMP7,o.4≥W
   │  DOWN2/I-5I7 ──────→      produce complete set of eigenvalues in Bn ...
   │  M=N                      and complete set of eigenvectors in Cn ...
  ┌──JUMP8
  │ →7)L=xINTPT(o.5Hn+I.6)
  │  DOWN3/I-5I7 ──────→      transform secular matrix to codiagonal form
  │  I=o
  │ →32)I=I+I
  │  DOWN5/I-5I7 ──────→      compute and store I'th eigenvalue and vector
  │  BnvBn+Gn
  │  CnvN+Cn
  │ ┌JUMP32,I≠L
  │ │x6(Xn)Eo,L
  │ │*£vE(L-2)-E(L-I)
  │ │JUMP33,£≥o.000001
  │ │Wn=Wn+Gn
  │ │L=L+I
  │ └JUMP32
  │
  │ →33)M=L-I
  └→8)Envo                    M = number of eigenvectors computed
    P=O
    VvH
```

```
      READ(G)
      JUMPII0,G≠Gn
      READ(H)
      EvN-Fn
      JUMPII4
II0)  JUMPII5,4.5≥G
      GvG-E
      READ(O)
      I=I(I)O
      READ(HI)
      REPEAT
      X7(D+Fn)HI,O
      EvO
      JUMPII7
II5)  EvEn
II7)  JUMPII4,I.5≥G
      Q=-I
      L=O
      O=O
      READ(K)
      AnvK
      JUMPII3,G≥3.5
      O=2
      JUMPI21
II3)  Q=K+Q
      R=L(I)Q
      READ(UR)
      READ(VR)
      JUMPII2,O≠O
      READ(DR)
      READ(GR)
II2)  REPEAT
      L=R+I
III)  O=O+I
      READ(K)
      DnvK
      JUMPI23,O≥3
      CnvK
      JUMPI22,O≥2
I21)  BnvK
I22)  JUMPII3,K≥I
      JUMPIII
I23)  JUMPII4,O≥K
      Q=Q+K
      R=L(I)Q
      READ(UR)
      REPEAT
II4)  ACROSS8/I

      PSA
      CLOSE
```

symmetry code No.

Meaning of G

0 No symmetry
1 No symmetrization
2 C_{2v}
3 C2h
4 D_{2h}
5 D_{nh} as C_{2v}
6 D_{nh} (etc) as C_{2h}
7 D_{nh} (etc) as D_{2h}

Read complete numerical description of the symmetry.

Programme 8

see FLOW CHART 3

```
TITLE
HUCKEL MOLECULAR ORBITALS AND DERIVED QUANTITIES
 CHAPTERI
```

This chapter is used in full only when degeneracies occur among the eigenvalues. Orbitals belonging to the symmetry species of the groups D_{2h}, C_{2v}, C_{2h} are derived from the arbitrary vectors produced by Programme -517 by a process equivalent to using projection operators. A maximum of 2 vectors of any one symmetry species may be found. Where more than 2-fold degeneracy occurs within any one symmetry species the later vectors are made orthogonal to the earlier ones without regard for symmetry; this produces vectors belonging to the symmetry species if there is not more than 2-fold degeneracy in more than one symmetry species at the same eigenvalue.

```
E→58
F→59
W→59
X→59
Y→59
Z→60
U→29
D→I4
G→I4
H→I3
A→3
B→3
C→7
V→29

→ 8)X6(Xn)Eo,M
  £v-I                          Read the eigenvalues from the auxiliary store
  Xv0.5
  EM=4
  W=Gn
  I=I(I)M                       W = degeneracy counter
  CHECK(EI,E(I-I),0.0000009,I0I)
  JUMPI03,W≥2                   Compare eigenvalues in pairs.
→ I04)REPEAT                    If equal go to 101) to count
                                degeneracy. If unequal but previous
   JUMPI02,G≠Gn                 pair equal go to 105 to symmetrize.
  I=0(I)5
  READ(CI)
  REPEAT                        abbreviated symmetry description
  GvH
  JUMPI06
→ I02)JUMPI09,An≥I.5
  UI=Uo
  VI=Vo
  DI=Do
→ I09)JUMPI06,I.5≥G
  Co=Uo
  CI=Vo
  C3=UI
  C4=VI                         generate abbreviated symmetry description
  C2=Do
  C5=DI
→ I06)HvWn
  ACROSS49/2 ——————→
```

```
101)WvW+Gn
    JUMP104,W≥3
    UvN1-N+F
    X6(U)F1,N
    JUMP104

103)?1=1
    S=0
    Y=En
    Z=En
    B=En
105)Bo=En
    B1=En
    B2=En
    B3=En
    L=1(1)180
    XL=En
    REPEAT
    JUMP107,G≥1.5
    Ho=En
    YvGn
    S=1
    X6(NB+U)W1,N
    JUMP55
107)JUMP23,3.5≥G
    T=XINTPT(An-X)
    J=3
    O=o(1)T
    K=XINTPT(UO)
    L=XINTPT(VO)
    Q=XINTPT(DO)
    R=XINTPT(GO)
    A=FK+FL+FQ+FR
    A=XA
    WK=A
    WL=A
    WQ=A
    WR=A
    A=XMOD(A)
    Bo=Bo+A
    A=FK-FL-FQ+FR
    A=XA
    XK=A
    XL=-A
    XQ=-A
    XR=A
    A=XMOD(A)
    B1=B1+A
    A=FK+FL-FQ-FR
    A=XA
    YK=A
    YL=A
    YQ=-A
    YR=-A
    A=XMOD(A)
    B2=B2+A
    A=FK-FL+FQ-FR
    A=XA
    ZK=A
    ZL=-A
    ZQ=A
    ZR=-A
    A=XMOD(A)
    B3=B3+A
    REPEAT
JUMP24
```

count degeneracy

read from auxiliary store first member of degenerate set of vectors.

Y = 1 if orthonormalization without symmetrization

for orthonormalization

Derive vectors belonging to the symmetry species of D_{2h} (four-fold positions only) from the arbitrary vector in F1 ... , by using appropriate projection operators.

SySz vector in W1 ...
AySz vector in X1 ...
SyAz vector in Y1 ...
AyAz vector in Z1 ...

```
      23)T=-1
         J=1
      24)C=En
         R=XINTPT(Bn)
         JUMP48,0≥R
      44)Q=T+1
         T=T+R
         O=Q(1)T
         K=XINTPT(UO)
         L=XINTPT(VO)
         A=FK+FL
         WK=A
         WL=A
         JUMP35,J≥3
         A=XMOD(A)
         Bo=Bo+A
      35)A=FK-FL
         JUMP36,J≥3
         Vn=XMOD(A)
         B1=B1+Vn
      36)JUMP42,En≥C
         YK=A
         YL=-A
         JUMP43
      42)XK=A
         XL=-A
      43)REPEAT
         JUMP45,C≥Gn
         JUMP45,1≥J

      48)R=XINTPT(Cn)
         JUMP45,0≥R
         C=Gn
         JUMP44

      45)L=XINTPT(Dn)
         JUMP49,0≥L
         Q=T+1
         T=T+L
         O=Q(1)T
         K=XINTPT(UO)
         WK=2FK
         REPEAT
```

As above for two-fold positions

S vector in W1 ...
A vector in X1 ... or Y1 ...

the atom at the origin (D_{2h} or C_{2h})
or
the atoms on the axis (C_{2v})

```
49)T=o(1)J
   JUMP51,o.ooooo5≥BT
   O=6oT
   JUMP70,Z≥Gn
47)HSvT
   S=S+1
70)K=O
   A=En
   L=1(1)N
   K=K+1
   A=WKWK+A
   REPEAT
   ?A=xSQRT(Gn/A)
   K=O
   L=1(1)N
   K=K+1
   WK=AWK
   REPEAT
   JUMP51,Z≥Gn
   JUMP67,En≥Y
   JUMP58,R≠Q
67)x7(NB+U)W(O+1),N
   BvB+Gn
   JUMP58,£≥Z
   JUMP108,B≥W
51)REPEAT

   JUMP55,Z≥Gn
57)Z=Gn
   x6(NS+U)F1,N
   JUMP105

55)Q=S-1
   R=o(1)Q
   x6(NR+U)F1,N
   T=xINTPT(HR)
   A=En
   O=6oT
   K=O
   J=1(1)N
   K=K+1
   A=A+FJWK
   REPEAT
   C=xMOD(A)
   JUMP58,C≥o.9999
   K=O
   J=1(1)N
   K=K+1
   WK=WK-AFJ
   REPEAT
   Z=£
   JUMP47
58)REPEAT
   JUMP108,B≥W
   JUMP28,Y≥Gn
   Y=Gn
   S=o
   A=Gn
66)HS=En
   AvGn+A
   S=S+1
   JUMP66,B≥A
   JUMP28
108)W=Gn
   JUMP104

   xSQRT
   PSA
   CLOSE
```

BT = 0 if the T'th symmetry species is absent

Z = 0 first time round
    1 second time round

Normalization of a vector of the T'th symmetry species

store normalized vector
count vectors stored

If two cycles completed

First member of original set of vectors not yet overwritten with a symmetrized one.

Take vectors found in second cycle - if different from those of same symmetry found in first cycle orthogonalize, if not reject.

if complete orthonormalized set has now been found

Programme H

```
TITLE
HYDROCARBONS - NO SYMMETRIZATION
                                        see FLOW CHART 4
CHAPTERo
 B→79
C→79
A→139
H→59
E→81
G→37

 10)HALT
300,0
12)627,0
14)600,32
 200,32
 370,31
 290(14)
 370,29
 280(12)

  Gnv1
 Envo                                   constants
 READ(N)                                N = number of atoms
 READ(R)                                R = number of bonds
 AnvEn
 Bnv4030
 L=o(I)319                              auxiliary storage datum
 AL=En
 REPEAT
 T=1-1
 K=320
 Q=o(I)T
 READ(BQ)                               bond list
 READ(CQ)
 1)AvNBQ-N+CQ-Gn-An                     position of matrix element for bond
 JUMP2,A≥320                            if beyond capacity of working store
 ?M=XINTPT(A)
 AM=Gn                                  set up matrix element
 JUMP3,Q≠T
 K=M+1
 2)x7(An)Ao,K                           store K elements of matrix
 AnvK+An
 JUMP3,319≥A
 M=M(-1)o
 AM=En
 REPEAT
 JUMP1
 3)REPEAT
```

PSA
CLOSE

```
XnvBn
YnvBn-R
ZnvYn-R
FvN+Xn
x7(Yn)Bo,R
x7(Zn)Co,R
READ(Un)
READ(O)
JUMP93,O=N
JUMP20,I00≥O
O=O-I00
C=Gn
JUMP2I
20)C=En
2I O=O-I
I=o(I)O
READ(HI)
REPEAT
JUMP92,En≥C
READ(J)
I=I(I)J
READ(E(I-I))
REPEAT
JUMP9I
92)T=R-I
I=o
J=o
Q=o(I)T
M=o
94)JUMP95,BQ≠HI
EJvQ+Gn
J=J+I
JUMP96,45≥J
JUMP9I
95)M=M+I
JUMP96,M>O
I=I+I
JUMP94,O≥I
I=o
JUMP94
96)REPEAT
9I)O=O+I
JUMP4
93)I=o(I)R
HI=I+I
EI=HI
REPEAT
J=R
4)DvZn-O
x7(D)Ho,O
HvJ
EvD-H
x7(E)Eo,J
FnvO
```

auxiliary store addresses

store bond list

output parameter for energy and coefficients
number of selected atoms
if O = N list of selected atoms consists of all atoms
if O <100 list of selected bonds must be generated

selected atoms

number of selected bonds

selected bonds

search bond list for those
whose first atom is in the list
of selected atoms. Such bonds
taken as selected bonds in Eo ...

selected atoms and bonds = all atoms and bonds

store selected atoms
H = number of selected atoms

store selected bonds
Fn = number of selected atoms

```
   !=503(1)507
   READ(B1)
   REPEAT
   U=XFRPT(Un)
   ?UvX+Y+Z+U
   X7(F+NN)H,7
   WvN
   CvWW-An
   JUMP9,479≥C
   J=479
   JUMP13
9) J=XINTPT(C-0.5)
13)L=0(1)J
   BL=En
   REPEAT
   T=J+1
6) JUMP5,C≥480
   T=XINTPT(C)
5) X7(An)B0,T
   AnvT+An
   Cv-T+C
   JUMP6,C≥0.5
   AnvEn
   An=X19(An,3,W)
   CnvF
   JUMP7,0.4≥U
   DOWN2/1-5I7
   M=N
   JUMP8
7) L=XINTPT(0.5N+1.6)
   DOWN3/1-5I7
   I=1(1)L
   DOWN5/1-5I7
   BnvBn+Gn
   CnvN+Cn
   REPEAT
   M=L
8) V=E
   P=R
   EnvO
   READ(G)
   HnvN
   EvEn
   HvEn
   JUMP11,1.5≥G
   !=0(1)5
   READ(G!)
   REPEAT
11)ACROSS8/1
    PSA
   CLOSE
   n
```

read V,W,X,Y,Z - output parameters for derived quantities

fill up end of secular matrix with zeros as necessary

set all the diagonal matrix elements to 5 (the zero)

diagonalize the matrix stored in An ... eigenvalues in Bn ..., vectors in Cn ...

transform secular matrix to codiagonal form

compute and store I'th eigenvalue and vector

symmetry code No.

abbreviated symmetry description

A52

Programme E

```
TITLE
HETEROMOLECULES  2 PARAMETERS   NO SYMMETRIZATION
TITLE
(USE WITH SHORT CHAPTER1)

 CHAPTER0
B→79                          see FLOW CHART 5
C→79
A→139
E→111
H→29
G→7
X→5
Y→23

10)HALT
Bnv4030
610(L)                        auxiliary storage datum
300,32
250(L)
210(L)                        examine handswitch 5: if set put L=32 (new parameters)
280(16)                                             otherwise L=0 (new molecule)
300,0
12)627,0
11)600,32
200,32
370,31
290(11)                       reproduce heading
370,29
280(12)

Gnv1
Envo
READ(N)
READ(P)                       N = number of atoms
Fvn+Bn                        P = number of bonds
T=P-1
Q=0(1)T
READ(*BQ)
READ(CQ)                      bond list
REPEAT
READ(S)
T=S-1                         number of heteroatoms
Q=0(1)T
READ(XQ)
REPEAT                        heteroatoms
XS=En
READ(S)
T=S-1                         number of heterobonds
Q=0(1)T
READ(YQ)
REPEAT                        heterobonds
YS=En
Q=T+8
X7(NN+F+7)Xo,Q                store Nos. of heteroatoms and heterobonds
JUMP15
16)Evv
X6(B1)Co,P
X6(Bo)Bo,P                    recover bond list (if repeating molecule
15)R=P                                           with new parameters h and k)
AnvEn
CvNN+F
X6(C+7)Xo,18                  recover Nos. of heteroatoms and heterobonds
```

```
READ(G)
READ(Y)
NEWLINE
620,I3
620,I3
620,30
Q=o(I)39
620,o
REPEAT
620,30
620,I3
620,27
620,
PRINT(G)3,4
620,30
620,I3
620,27
620,II
PRINT(Y)3,4
C=o.I
Q=o(I)28I
AQ=En
REPEAT
T=R-I
K=282
I=o
Q=o(I)T
Wvq+Gn
Z=Gn
JUMPI,W≠YI
I=I+I
Z=Y
I)AvNBQ-N+CQ-Gn-An
JUMP2,A≥282
?M=XINTPT(A)
AM=Z
JUMP3,T≠Q
K=M+I
2)X7(An)Ao,K
AnvK+An
JUMP3,28I≥A
M=M(-I)o
AM=En
REPEAT
JUMPI
3)REPEAT
```

'H'

print value of h

'K'

print value of k

Z = value of matrix element

position of the matrix element

value of the element

store K matrix elements

set up elements of the secular matrix corresponding to each bond.

```
XnvBn
YnvBn-R
ZnvYn-R
JUMP17,L≠0

 X7(Yn)Bo,R
X7(Zn)Co,R
READ(Un)
READ(O)
JUMP93,O=N
JUMP20,100≥O
O=O-100
W=Gn
JUMP21
20)W=En
21)O=O-1
I=o(1)O
READ(HI)
REPEAT
JUMP92,En≥W
READ(J)
I=1(1)J
READ(E(I-1))
REPEAT
JUMP91
92)T=R-1
I=o
J=o
Q=o(1)T
M=o
94)JUMP95,BQ≠HI
EJvQ+Gn
J=J+1
JUMP96,45≥J
JUMP91
95)M=M+1
JUMP96,M>O
I=I+1
JUMP94,O≥I
I=o
JUMP94
96)REPEAT
91)O=O+1
*DvZn-O
X7(D)Ho,O
97)HvJ
EvD-H
X7(E)Eo,J
JUMP4
93)HvR
4)FnvO
```

auxiliary store addresses

store bond list

output parameter for energy and coefficients
number of selected atoms
if Q = N no list of selected atoms is defined
if Q <100 list of selected bonds must be generated

selected atoms

number of selected bonds

selected bonds

search bond list for those whose first atom is in the list of selected atoms; such bonds taken as selected bonds in Eo ...

store selected atoms
H = number of selected bonds

Fn = number of selected atoms.

```
I=503(I)507
READ(BI)
REPEAT                          read V,?,X,Y,Z - output parameters for
U=Un+C                                           derived quantities
X7(C)H,7
I7)X6(C+Gn)Un,I                 store output parameters
X6(C+4)X,3
U=XFPPT(Un)                     recover output parameters
?UvX+Z+Y+U
WvN
CvWW-An
JUMP9,449≥C
J=449
JUMPI3
9)J=XINTPT(C-0.5)
I3)Q=o(I)J
BQ=En                           fill up end of secular matrix with zeros
REPEAT                            as necessary
T=J+I
6)JUMP5,C≥450
T=XINTPT(C)
5)X7(An)Bo,T
AnvT+An
Cv-T+C
JUMP6,C≥0.5
AnvEn
T=N-I
I=o
Q=o(I)T
VvQ+Gn
JUMPI9,V≠XI
I=I+I
BQ=3+G
JUMP23
I9)BQ=3                         prepare vector of diagonal elements
23)REPEAT
X7(Bn)Bo,N
An=X2I(An,Bn,W)
CnvF                                    insert diagonal into matrix

JUMP7,0.4≥U
DOWN2/I-5I7 ------------------>
M=N                             diagonalize the matrix in An ...
JUMP8                           putting eigenvalues in Bn..., vectors in Cn ...
7)O=XINTPT(0.5N+I.6)
DOWN3/I-5I7 ------------------>
I=I(I)O                         transform secular matrix to codiagonal form
DOWN5/I-5I7 ------------------>
BnvBn+Gn                        compute and store I'th eigenvalue and vector.
CnvN+Cn
REPEAT
'=0
8)ACROSS9/I ------------------>
PSA
CLOSE
```

Programmes H and E

```
TITLE
HUCKEL MOLECULAR ORBITALS AND DERIVED QUANTITIES   POOLE MI24
TITLE
(SHORT CHAPTER 1)
```

see FLOW CHART 6

```
 CHAPTER1
 E→58
F→59
W→240
U→73
A→7
C→7
V→29

9)VvE
Envo
P=R
EvEn
HvEn
CvNN+F+25
JUMP14,o≥L
x6(C)Co,8
GvC6
HnvC7
JUMP8
14)READ(Hn)
READ(G)
JUMP98,1.5≥G
I=o(1)5
READ(CI)
REPEAT
98)C7vHn
C6vG
x7(C)Co,8
```

Entry from E chapter 0

recover abbreviated symmetry description, etc.,

number of π-electrons
symmetry code No.

abbreviated symmetry description

store abbreviated symmetry description, etc.

Programmes H and E

```
TITLE
HUCKEL MOLECULAR ORBITALS AND DERIVED QUANTITIES   POOLE MI24
TITLE
(SHORT CHAPTER 1)
                                                    see FLOW CHART 6
 CHAPTER1
 E→58
F→59
W→240
U→73
A→7
C→7
V→29

→ 9)VvE
Envo                                  Entry from E chapter 0
P=R
EvEn
HvEn
CvNN+F+25
JUMP14,0≥L
X6(E)C0,8
GvC6                                  recover abbreviated symmetry description, etc.,
HnvC7
JUMP8
→14)READ(Hn)
READ(G)                               number of π-electrons
JUMP98,1.5≥G                          symmetry code No.
I=0(1)5
READ(CI)
REPEAT
→98)C7vHn                             abbreviated symmetry description
C6vG
X7(E)C0,8                             store abbreviated symmetry description, etc.
```

Orthonormalization: this part of the programme is redundant if a version of Programme -517 with orthonormalization is used.

```
8)X6(XN)E0,M
  XV0.5
  S=0
  EM=4
  I=1(1)M
  CHECK(EI,E(I-1),0.000001,101)
  JUMP103,S≥1
104)REPEAT
```

look for degeneracies

```
  ACROSS49/2

101)S=S+1
  JUMP104
102)O=NS+N
  X6(NI-O+F)FI,O
  T=1(1)S
```

transfer set of degenerate orbitals from auxiliary store.

```
  O=T-1
  K=1
  J=NT+1
  R=0(1)O
  AR=EM
  L=1(1)N
  AR=AR+FJFK
  J=J+1
  K=K+1
  REPEAT
  J=J-N
  REPEAT
  K=1
  R=0(1)
  L=1(1)N
  FJ=FJ-ARFK
  J=J+1
  K=K+1
  REPEAT
  J=J-N
  REPEAT
```

form scalar products of last orbitals of current subset with all others in the subset.

subtract projections of last orbital on earlier ones.

```
  A=EM
  L=1(1)N
  A=A+FJFJ
  J=J+1
  REPEAT
  A=XSQRT(GM/A)
  J=J-N
```

renormalize

```
  L=1(1)N
  FJ=AFJ
  J=J+1
  REPEAT
REPEAT
  I=NS
  J=N+1
  X7(NI-O+F)FJ,O
  J=1
  S=0
JUMP104
```

store orthonormalized set

```
  XSQRT
PSA
CLOSE
```

Programme C

```
TITLE
C2V OR C2H  FACTORED DETERMINANT

CHAPTERo
VARIABLESI                          see FLOW CHART 7

10)HALT
11)600(I)
   JUMP11, I≥31
   JUMP12, I=32                     reproduce heading
   630(I)
   JUMP11

12)READ(G)                          G = symmetry code No.  (2 = C2v, 3 = C2h)
   READ(O)                          O = number of sets of heteroatoms
   JUMP111, O=-1
   READ(C)                          C = number of π-electrons
111)READ(L)                         number of general pairs of atoms
   M=L
   WL
   Q=L-1
   R=o(1)Q
   READ(UR)                         pairs of atoms in general positions
   READ(VR)
   REPEAT
   READ(K)
   ZK
   N=K+L
   JUMP114, o≥K
   R=Q+1
   O=O+K
   L=R(1)Q
   READ(UL)                         atoms on the symmetry element
   REPEAT
114)JUMP115, O≠-1
   CW+W+Z
115)S=-1
   READ(J)
   Ao=J
   JUMP118, o≥J
   L=1(1)J
   S=S+1
   READ(WS)                         atom pairs internally bonded
   JUMP117, -1≥0
   READ(DS)                         k_rs for internal bond
117)REPEAT
118)JUMP113, o≥O
   L=1(1)O
   S=S+1                                sets of heteroatoms
   READ(WS)                             h_r for heteroatom
   READ(DS)
   REPEAT
113)R=-1
   I=o(1)2
   READ(J)
   *BI=J
   JUMP119, o≥J
   L=1(1)J
   R=R+1
   READ(FR)                         external bonds
   READ(HR)
   JUMP116, -1≥0
   READ(GR)                         k_rs
116)REPEAT
119)REPEAT
```

```
READ(Un)
READ(Vn)
READ(Wn)
READ(Xn)
READ(Yn)
READ(Zn)
DnvXFRPT(Un)
?DnvDn+Xn+Yn+Zn

Envo
Gnv1
Xvo.5
Yv-3
Hv1.4142356
AnvEn
Bnv1000
Cnv1100
Fv4000
X7(F)Xn,3
FnvN
XnvF-M-Fn
DvF-Y
X7(D)Vo,256

I=o
J=o
A=Gn
B=Bo
JUMP54,En≥Bo
K)=41)
JUMP40
41)ZJ=VL
£J=VQ
J=J+1
JUMP40,B≥A
54)JUMP55,En≥B1
BvB1+B
K)=42)
JUMP40
42)JUMP57,2.5≥G
E(I-1)=VL
ZJ=UL
£J=VQ
J=J+1
57)JUMP40,B≥A
55)JUMP56,En≥B2
BvB2+B
K)=43)
JUMP40
43)ZJ=VL
£J=UQ
J=J+1
JUMP40,B≥A
JUMP56
40)L=XINTPT(FI)
Q=XINTPT(HI)
EI=UL
GI=UQ
I=I+1
AvGn+A
JUMP(K)
```

output parameters for derived quantities

constants

auxiliary storage addresses for eigenvalues
and eigenvectors of S matrix.
Datum for all other auxiliary storage.

generate complete bond list:

(external bonds)

```
56)Q=0
  JUMP38,Fn≥A0
  A=Gn
30)L=XINTPT(WQ)
  EI=UL
  GI=VL
  Q=Q+1
  I=I+1
  AvGn+A
  JUMP30,A0≥A

38)HnvI                          (internal bonds)
  FvJ+Hn
  YnvXn-E
  ZnvYn-E
  K=J-1
  L=0(1)K
  Q=L+I
  JUMP31,ZL≥£L                   arrange bonds to have lower
  FQ=ZL                           atom No. first
  £Q=£L
  JUMP32
31)FQ=£L
  £Q=ZL
32)REPEAT
  K=I-1
  L=0(1)K
  JUMP33,EL≥GL
  £L=GL
  JUMP34
33)£L=EL
  EL=GL
34)REPEAT
  K=K+J
  L=0(1)K
  ELvEL+0.001£L
  REPEAT
  T=72
  L=K(-1)0
  Q=XMAX(F0,0,K)                 put bonds in 'dictionary order'
  JUMP35,Q≥I
  T=T-1
  ZTvL+Gn
35)FL=FQ
  DL=£Q
  FQ=Fn
  REPEAT
  K=K+1
  X7(Yn)F0,K                     store reordered bond list
  X7(Zn)D0,K
  X6(D)V0,256
  DvD+%44
  X7(Zn-Fn)U0,N                  store selected atoms
  VvZn-Fn-Hn
  X7(V)ZT,I                      store selected bonds
  ACROSS19/1

  PSA
  CLOSE
```

Programme C see FLOW CHART 8

```
TITLE
HUCKEL MOLECULAR ORBITALS AND DERIVED QUANTITIES - 1/5.2 POOLE MI24
CHAPTER1

F→65
X→1
Y→2
V→30
D→35
U→36
G→30
F→46
H→46
W→35
A→0
B→2
C→67
Z→71

19)X0=Gn
Y0=Gn
Y1=Gn
Y2=H
L=N
JUMP9

20)N=M
X0=-Gn
Y1=X0
Y2=Y
JUMP9,G≥2.5
Y1=Y
9)?UVN
J=0
Q=N-1
Q=Q(-1)0
ZQ=-Y
REPEAT

JUMP13,0≥0
O=0
JUMP24,-1≥S
Q=0(1)S
DQ=Gn
REPEAT
24)Q=0(1)R
GQ=Gn
REPEAT
13)JUMP14,-1≥S
K=XINTPT(A0)
T=0(1)S
Q=XINTPT(WJ)
JUMP11,Q≥N
JUMP12,T≥K
ZQ=ZQ+X0DJ
JUMP15
12)ZQ=ZQ+DJ
15)J=J+1
11)REPEAT
14)J=0
I=0(1)2
JUMP3,Y≥YI
Q=XINTPT(BI)
4)JUMP3,0≥Q
EJVUFJ+HJ
FJ=YIGJ
J=J+1
Q=Q-1
JUMP4
3)REPEAT
```

Constants from Chapter 0:
Gn = 1
En = 0
X = 0.5
Y = -3
H = $\sqrt{2}$

Values of matrix elements for different types of bonds (S Matrix)

Values of matrix elents for different types of bonds (A Matrix)

Diagonal elements set to 'zero' = 3

set all k_{rs} = 1 for hydrocarbon

Prepare vector of diagonal matrix elements in Zo ...

Non-diagonal elements: positions in £o ...
values in Eo ...

```
PRESERVE
DvUU
R=o
T=37 1
BvT
I=o
16)S=T-1
S=S(-1)o
XS=En
REPEAT
JUMP38,o≥J
L=J-1
J=o
K=o(1)L
S=xINTPT(£K)
JUMP5,S≥T
XS=FK
JUMP6
5)£J=£K-B
FJ=FK
J=J+1
6)REPEAT
JUMP7,J≠o
38)JUMP7,D≥B
T=xINTPT(D)
7)XR=ZI
R=R+N+1
I=I+1
JUMP7,T>R
X7(An)Xo,T
JUMP35,I≥N
AnvAn+B
R=R-T
DvD-B
JUMP16
35)AnvEn
DOWN2/1-5117
RESTORE
JUMP23,En≥Y2
BnvU+Bn+Gn
CnvUU+Cn
JUMP20
23)Q=o
Yo=L
Y1=M
?N=L+M
J=N+1
X6(1000)Fo,J
FL=Y
FJ=Y
XovI100
X1vXo+YoYo
R=L+1
K=N-1
J=o
81)JUMP80,FR≥FQ
ZJvEn
FJvFQ+Y
Q=Q+1
JUMP82
80)ZJvGn
FJvFR+Y
R=R+1
82)J=J+1
JUMP81,K≥J
X7(Xn)Fo,J
```

D = number of elements in matrix

B = T = maximum number of elements that may be held in working store at once.

Clear space for matrix.

examine position: if ≥T reduce by B and store for the next block of the matrix. Otherwise set up matrix element.

D = number of elements still to be stored

insert diagonal elements

store T elements

prepare for next block

find eigenvalues and eigenvectors of matrix stored in An ...

Auxiliary store locations for eigenvalues and eigenvectors of A matrix.

total number of atomic orbitals

recover eigenvalues

Xo = address of first element of first S vector
X1 = address of first element of first A vector

place eigenvalues in order in Eo ... , symmetry in Zo ... (0 = S, 1 = A).

store eigenvalues

```
   JUMP72,Dn≥0.4
   K=XINTPT(CX-0.4)
71)£vFK-F(K+1)
   JUMP72,£>0.00001
   K=K+1
   JUMP71
72)DnvF
   YvXH
   HvK+Gn
   X6(F)An,3
   X7(NN+F)Hn,4
   X7(NN+F+4)An,3
   Hn=C
```

compute K = number of eigenvectors wanted -1

number of π-electrons

```
   J=0(1)K
   L=1(1)N
   FL=Fn
   REPEAT
   I=XINTPT(ZJ)
   O=XINTPT(YI)
   X6(XI)£0,O
   P=XINTPT(U-X)
   L=0(1)P
   R=XINTPT(UL)
   Q=XINTPT(VL)
   FR=Y£L
   JUMP73,I≠1
   FQ=-FR
   JUMP74
73)FQ=FR
74)REPEAT
   JUMP67,I≠0
   T=XINTPT(Z)
   JUMP67,0≥T
   L=P+1
   P=P+T
   L=L(1)P
   R=XINTPT(UL)
   FR=£L
   REPEAT
67)X7(Dn)F1,N
   DnvN+Dn
   XIvXI+YI
   REPEAT
```

clear space for 'long' eigenvector coefficients

symmetry
order of 'short' vector
short vector

pairs of atoms in general positions

atoms on the symmetry element

store 'long' vector

take eigenvectors expressed in terms of symmetry orbitals ('short') and express them in terms of atomic orbitals ('long')

```
   M=K
   P=XINTPT(F)
   EvEn
   ACROSS49/2 ⟶
```

P = total number of bonds

```
   PSA
   CLOSE
```

Programme D

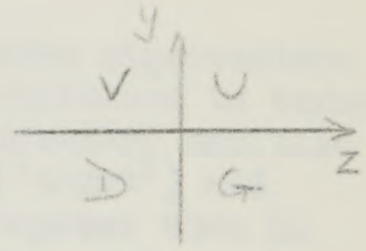
```
TITLE
D2H - FACTORED DETERMINANT

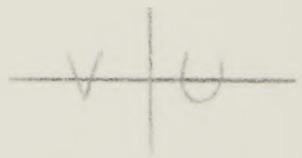
CHAPTERo                          see FLOW CHART 9

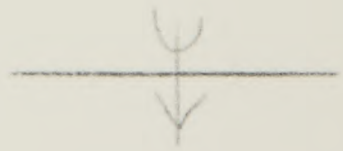
VARIABLES 1


10)HALT
300,0
12)627,0
11)600,32
200,32                            reproduce heading
370,31
290(11)
370,29
280(12)

READ(K)                           sets of atoms in general positions
P=K
CvK
Q=K-1
L=0(1)Q
READ(UL)
READ(VL)                          sets of 4 atom Nos.
READ(DL)
READ(GL)
REPEAT
READ(L)                           pairs on the z-axis
M=P+L
WvL
JUMP112,0≥L
R=K(1)Q
READ(UR)                          pairs of atom Nos.
READ(VR)
REPEAT
112)READ(K)                       pairs on the y-axis
N=M+K
O=P+K
EvK
JUMP113,0≥K
R=Q+1
Q=Q+K
L=R(1)Q
READ(UL)                          pairs of atom Nos.
READ(VL)
REPEAT
113)READ(L)                       atom at the origin
N=L+N
ZvL
JUMP114,0≥L
R=Q+1
Q=Q+L
K=R(1)Q
READ(UK)                          atom No.
REPEAT
114)S=-1
I=0(1)4
READ(J)                           number of internal bonds of type I
AI=J
JUMP118,0≥J
L=1(1)J
S=S+1
READ(WS)                          internally bonded sets
REPEAT
118)REPEAT
```









```
R=-1
I=0(1)7
READ(J)
BI=J                                   number of external bonds of type I
JUMP 119, 0≥J
L=1(1)J
R=R+1
READ(FR)
READ(HR)                               externally bonded sets
REPEAT
119)REPEAT
I=488(1)493
READ(EI)
REPEAT                                 output parameters for derived quantities
Dn=XFRPT(Un)
D?nvDn+Xn+Yn+Zn
Envo
Gnv1
Xvo.5
Yv-3                                   constants
Hv1.414213562

AnvEn
Bnv1000
Cnv1100                                auxiliary store addresses for eigenvalues
Fv4090                                 and eigenvectors of SySz matrix.
*X7(F)Xn,3                             datum for other auxiliary storage
FnvN
K=M+N*+O+P                             K = total number of atoms
Xnv-K+F
DvXn-Fn
X7(D)Uo,N                              store selected atoms
102,0
103,0                                  Bond-list generating routine:
B=Ao
A=Gn                                   Selected bonds (those in first quadrant of the xz plane) set up in Bo-Co, others in Zo-Eo.
JUMP 51,En≥Ao
111,1
590(30)
590(39)
30)402(Wo)
440,31.62
410,32
004,32+                                subroutine for the selected bond of each set (internal)
404(Uo)
412(Eo)
404(Vo)
412(C)
122,1
AvGn+A
591,0

39)404(Go)
412(H39)
404(Vo)
413(Zo)
404(Do)
413(Eo)
123,1
JUMP 30,B≥A
51)JUMP 52,En≥A1                       internal bonds
BvA1+B
111,1
590(30)
404(Do)
413(Zo)
404(Go)
413(Eo)
123,1
JUMP 30,B≥A
52)EvA2+A3+A4
```

```
JUMP 38, En>£
Bv£+B
III, I
590(30)
JUMP 30, B≥A
JUMP 38, En≥A4
404(Vo)
413(Zo)
404(Do)
413(£o)
413(Z1)
404(Go)
413(£1)
413(Z2)
404(Uo)
413(£2)
123, 3

38) 106, o
A=Gn
B=Bo
JUMP 54, En≥Bo
III, I
590(40)

404(Vo)
413(Zo)
405(Vo)
413(£o)
404(Do)
413(Z1)
405(Do)
413(£1)
404(Go)
405(Go)
413(£2)
123, 3
JUMP 40, B≥A
54) £vB1+B2
JUMP 55, En≥£
Bv£+B
III, I
590(40)
404(Vo)
413(Zo)
405(Vo)
413(£o)
123, I
JUMP 40, B≥A
55) JUMP 56, En≥B3
BvB3+B
III, I
590(40)
404(Go)
413(Zo)
405(Uo)
413(£o)
404(Vo)
413(Z1)
405(Vo)
413(£1)
404(Do)
413(Z2)
405(Vo)
413(£2)
123, 3
JUMP 40, B≥A
```



(internal bonds, contd.)

Bond-list generating routine



(external bonds)

```
56) JUMP 57, En≥B4
    BvB4+B
    III, I
    590(40)
    404(Vo)
    413(Zo)
    405(Uo)
    413(£o)
    404(Do)
    413(Z1)
    405(V*o)
    413(£1)
    413(£2)
    404(Go)
    413(Z2)
    123, 3
    JUMP 40, B≥A
57) £vB5+B6+B7
    JUMP 58, En≥£
    Bv£+B
    III, I
    590(40)
    404(Vo)
    413(Zo)
    405(Uo)
    413(£o)
    123, I
    JUMP 40, B≥A
    JUMP 58, En≥B7
    404(Uo)
    413(Zo)
    405(Vo)
    413(£o)
    413(£1)
    404(Vo)
    413(Z1)
    123, 2
    590(58)

40) 406(Fo)
    440, 31.62
    410, 32
    004, 32+
    406(Ho)
    440, 31.62
    410, 32
    005, 32+
    404(Uo)
    412(Eo)
    405(Uo)
    412(Co)
    126, I
    122, I
    AvGn+A
    591, 0

58) 0121(I)
    0133(J)
    ?J=J
    ?I=I
    HnvI
    GvJ+Hn
    YnvD-G
    ZnvYn-G
    VvZn-Hn
    X7(*Yn)Eo, I
    X7(Zn)Co, I
    X7(Hn+Yn)Zo, J
    X7(Hn+Zn)£o, J
    ACROSS19/1 ------>

    PSA
    CLOSE
```

Bond-list generating routine (contd.)

(external bonds, contd.)

subroutine for the selected bond of each set (external)

Hn = number of selected bonds
G = total number of bonds
Auxiliary store addresses for bond-list

store bond-list

Programme D

```
TITLE
HUCKEL MOLECULAR ORBITALS AND DERIVED QUANTITIES - 1/5 POOLE MI24
CHAPTER1

E→56
X→4
Y→7
V→39
F→39
H→39
C→39
A→4
B→7
W→11
D→19
G→19
U→40
£→71
Z→71

→19)400(Gn)
 410(X0)
 410(X1)
 410(X2)
 410(X3)
 410(Y0)
 410(Y1)
 410(Y2)
 440(Gn)
 410(X4)
 410(Y7)
 400(H)
 410(Y3)
 410(Y4)
 410(Y5)
 410(Y6)
 L=N
 T)=20)
 JUMP9

→20)N=M
 400(En)
 410(X4)
 450(Gn)
 410(X2)
 410(X1)
 400(Y)
 410(X3)
 410(Y2)
 410(Y4)
 410(Y5)
 410(Y6)
 410(Y7)
 T)=21)
 JUMP9

→21)BvC+W-Gn
 JUMP24,-1≥S
 J=0(1)S
 JUMP25,B≥WJ
 WJvWJ-W
→25)REPEAT
→24)J=0(1)R
 JUMP26,B≥FJ
 FJvFJ-W
→26)JUMP27,B≥HJ
 HJvHJ-W
→27)REPEAT
```

see FLOW CHART 10

Constants from Chapter 0

Gn = 1
En = 0
X = 0.5
Y = -3
H = √2

values of matrix elements for different types of bonds (SySz matrix)

(set	X0	Y0		1	1
	X1	Y1		1	1
	X2	Y2		1	1
	X3	Y3	=	1	√2
	X4	Y4		2	√2
		Y5			√2
		Y6			√2
		Y7			2)

order of SySz matrix

order of AySz matrix

(reset	X0	Y0		1	1	
	X1	Y1		-1	1	
	X2	Y2		-1	-3	(-3 signifies
	X3	Y3	=	-3	√2	that this
	X4	Y4		0	-3	bond is not
		Y5			-3	
		Y6			-3	
		Y7			-3)	

renumber functions derived from atoms on the y-axis for matrices where those on the z-axis will not appear.

```
N=0
400(XI)
410(Xo)
410(X3)
400(Gn)
410(XI)
410(Y2)
400(H)
410(Y4)
400(Y)
410(X2)
410(YI)
410(Y3)
T)=22)
JUMP9

22)N=P
400(Xo)
410(XI)
440(Xo)
410(X4)
400(Y)
410(Y2)
410(Y4)
410(X3)
T)=23)

9)UvN?
J=o
Q=N-I
Q=Q(-I)o
ZQ=-Y
REPEAT
I=o(I)4
JUMPII,Y≥XI
AvEn
2)JUMPI,A≥AI
Q=XINTPT(WJ)
ZQ=ZQ+XI
J=J+I
AvA+Gn
JUMP2
II)Q=XINTPT(AI)
J=J+Q
I)REPEAT
J=o
K=o
I=o(I)7
JUMPI3,Y≥YI
AvEn
4)JUMP3,A≥BI
£JvUFK+HK
EJ=YI
J=J+I
K=K+I
AvA+Gn
JUMP4
I3)Q=XINTPT(BI)
K=K+Q
3)REPEAT
```

order of SyAz matrix

```
(reset  Xo  Yo        -1    1
        X1  Y1         1   -3
        X2  Y2        -3    1
        X3  Y3   =    -1   -3
        X4  Y4         0   √2
            Y5             -3
            Y6             -3
            Y7             -3)
```

order of AyAz matrix

```
(reset  Xo  Yo        -1    1
        X1  Y1        -1   -3
        X2  X2        -3   -3
        X3  Y3   =    -3   -3
        X4  Y4        -2   -3
            Y5             -3
            Y6             -3
            Y7             -3
```

diagonal elements set to 'zero' = 3

omit bond if XI = -3

prepare vector of diagonal matrix elements in Zo ...

omit bond if YI = -3

off-diagonal elements : positions in £o ...
values in Eo ...

subroutine to set up a matrix in the auxiliary store at An ...
given diagonal elements as Zo ..., off-diagonal elements in £o..., Eo...

```
      PRESERVE
      DvUU                    D = total number of elements in the matrix
      R=o
      T=279
      BvT                     B * T = maximum number of elements that may be
      I=o                             held in working store at any one time
→16)S=T-I
   ┌─S=S(-I)o
   │  XS=En                  clear space for matrix elements
   └─REPEAT
  ┌──JUMP38,o≥J
  │   L=J-I
  │   J=o
  │ ┌K=o(I)L
  │ │ S=XINTPT(£K)          examine position: if ≥T reduce by B and store
  │ │ ┌JUMP5,S≥T              for next block of matrix.  Otherwise set up
  │ │ │ XS=EK                 matrix element.
  │ │ │ JUMP6
  │ │ └→5)£Jv£K-B
  │ │   EJ=EK
  │ │   J=J+I
  │ └→6)REPEAT
  │   ┌JUMP7,J≠o
  └→38)JUMP7,D≥B
    T=XINTPT(D)             D = number of elements still to be stored
  ┌→7)XR=ZI
  │ R=R+N+I                 insert diagonal elements
  │ I=I+I
  └─JUMP7,T>R
    X7(An)Xo,T              store T elements
  ┌─JUMP35,I≥N
  │ AnvAn+B
  │ R=R-T                   prepare for next block
  │ DvD-B
  ├─JUMP16
  └→35)AnvEn
    DOWN2/I-517 ──────────→ diagonalize matrix stored in An ...
    RESTORE

    BnvU+Bn+Gn              auxiliary store addresses for eigenvalues and
    CnvUU+Cn                  eigenvectors of next matrix
    JUMP(T)
```

```
23)Q=0                    index for SySz eigenvalues
R=L+1                     index for AySz eigenvalues
S=R+M+1                   index for SyAz eigenvalues
T=O+S+1                   index for AyAz eigenvalues
J=T+P
?N=J-3                    total number of atomic orbitals

X6(1000)Fo,J              eigenvalues in four blocks with gaps between
FL=Y
F(S-1)=Y
F(T-1)=Y                  fill in gaps with 'flags' of -3
FJ=Y
YovL
Y1vM                      orders of the four matrices
Y2vO
Y3vP
XovI100                   address of first SySz vactor
X1vXo+YoYo                address of first AySz vector
X2vX1+Y1Y1                address of first SyAz vector
X3vX2+Y2Y2                address of first AyAz vector
JUMP56,Dn≥0.4
K=XINTPT(NX-0.4)          K = number of eigenvectors required - 1
JUMP57
56)K=N-1
57)Ao=Fo                  first eigenvalue of each symmetry
A1=FR
A2=FS
A3=FT
J=o
50)I=XMAX(Ao,o,3)         symmetry of vector of highest eigenvalue
ZJ=I
EJ=AI+Y
J=J+1
002(I)
202(Q)                    place eigenvalues in order in Eo ...
320,1                     noting symmetry of each in Zo ...
407(Fo)
412(Ao)
212(Q)
JUMP50,K≥J
X7(Xn)Eo,J                store reordered eigenvalues
X6(F)An,3
DnvF
YvXH

400(Gn)
410(Ao)
410(Bo)
410(B4)
410(B5)
410(A2)
410(B3)
400(En)                   prepare multipliers for generation of 'long'
450(Gn)                   eigenvectors (in terms of atomic orbitals)
410(A1)                   from the 'short' ones (in terms of symmetry
410(B1)                   orbitals) which have been found.
410(B2)
410(B6)
410(A3)
410(B7)
```

```
      J=o(1)K
        Q=1(1)N
        FQ=En                    clear space for 'long' eigenvector
        REPEAT
        I=XINTPT(ZJ)             symmetry
        O=XINTPT(YI)             order of 'short' vector
        X6(XI)£o,O               short vector
        P=XINTPT(C-X)            C = number of sets of 4 atoms in general positions
        L=o(1)P
        Q=XINTPT(UL)
        R=XINTPT(VL)             atom Nos.
        S=XINTPT(DL)
        T=XINTPT(GL)
        FQ=X£L
        FR=AIFQ                  coefficients for 'long' vector
        FS=BIFQ
        FT=B(I+4)FQ
        REPEAT
        T=XINTPT(W)              W = number of pairs on
      JUMP60,o≥T                     z-axis
        S=P+1
        P=P+T
      JUMP60,I≥2
        S=S(1)P
    63) L=S
    64) Q=XINTPT(US)
        R=XINTPT(VS)
        FQ=Y£L
        JUMP61,I≥1
        FR=FQ
        JUMP65
    61) FR=-FQ
    65) JUMP66,o≥O
        REPEAT

    60) O=XINTPT(E)              E = number of pairs on
      JUMP62,o≥O                     y-axis
        S=P+1
        P=P+O
      JUMP62,I≥3
        JUMP70,I≥2
      JUMP62,I≠o

    70) O=o
        S=S(1)P
      JUMP63,I≠2
        L=S-T
        JUMP64
    66) REPEAT

    62) JUMP67,En≥Z              atom at the origin
        JUMP67,I≠o
        T=XINTPT(U(P+1))
        FT=£(L+1)
    67) X7(Dn)F1,N               store 'long' vector
        DnvN+Dn                  auxiliary store address for next vector
        XIvXI+YI                 auxiliary store address of next short
      REPEAT                       vector of symmetry I.

        M=K                      number of vectors stored
        EvEn
        P=XINTPT(G)              total number of bonds
        Gv4
        HvEn
        £vNN+F
        X7(£)Hn,4
        CvN                      number of π-electrons
        X7(£+G)An,3
        ACROSS 49/2 ------------>
        PSA
        CLOSE
```

take eigenvectors expressed in terms of symmetry orbitals (short) and express them in terms of atomic orbitals (long).

see flow chart 2.

```
CHAPTER2
VARIABLES1
 49)I=0(1)30
620,0                          punch 3 inches of blank tape
REPEAT

 U=XFRPT(Un)
R=XINTPT(H)                    R = number of orbitals to be tabulated
JUMP79,0.4≥Un
Y=0.000005
Q=R-1
I=0(1)Q
EI=EI-3                        subtract the energy zero
REPEAT
K=XINTPT(HnX)
A=XFRPT(Un+Un)
S=0                            S = 0  orbital energies to be tabulated
JUMP44,Un≥0.7                  S = 1  total π-energy only to be printed
S=1
JUMP47
44)JUMP50,1.7≥Un
620,30
620,30
620,13
620,13
620,27
620,5                          'ENERGY
620,14                                S = 0'
620,5
620,18
620,7
620,25
620,0
620,13
620,14
620,27
620,19
620,0
620,10
620,16                                        'S = 0.25'
620,28
620,2
620,21
47)VnvHn-K-K
U=En
Z=En
I=0(1)Q
JUMP45,S≠0
620,30
620,13                         Print energy parameters m_j (EI)
PRINT(I+1)2,0                  and, if A = 0, k_j (WI)
PRINT(EI)1,7
45)£=Gn+XXEI
WI=EI/£
JUMP57,I≥K
U=U+EI
Z=Z+WI
57)JUMP46,S≠0
JUMP46,A≥Y
PRINT(WI)1,7
46)REPEAT
```

```
JUMP48,En≥Vn
U=U+XEK
Z=Z+XWK
48)620,30
620,I3
620,I3
620,27
620,20
620,I5
620,20
620,I
620,I2
620,0
620,I4                    'TOTAL PI ENERGY'
620,27
620,I6
620,9
620,0
620,I4
620,27
620,5
620,I4
620,5
620,I8
620,7
620,25
NEWLINE
PRINT(U+U)6,7
JUMP62,A≥Y
PRINT(Z+Z)I,7             print total π-energy
62)JUMP79,2.7≥Un

 50)620,30
620,I3
620,I3
620,27
620,3
620,I5
620,5
620,6
620,6
620,9
620,3                     'COEFFICIENTS'
620,9
620,5
620,I4
620,20
620,I9
620,0
O=XINTPT(Fn+E)
JUMP88,O≥N                Q = total number of selected atoms
X6(D)Vo,O
88)T=o                    selected atoms
C=En
5I)620,30
620,I3
55)JUMP53,5≥R
K=6
JUMP52
53)K=R
52)Q=KN
X6(F+C)FI,Q
620,I4
620,I4
L=I(I)K
PRINT(6T+L)7,o
REPEAT                    print orbital Nos. to head columns
620,30
620,I3
620,27
620,5
620,0                     'E'
620,I4
620,I4
620,I4
620,I4
```

```
      K=K-1
      L=o(1)K
      I=6T+L
      PRINT(EI)1,5                    print energy parameters
      REPEAT
      620,30
      620,13
      JUMP59,1.5≥G
      620,14
      620,14
      620,14
      620,14
   74)L=o(1)K
      620,14                          cycle for printing symmetry labels
      BvLN
      Q=6
      S=o
   72)I=xINTPT(B+CS)
      J=xINTPT(B+C(S+1))              test pairs of orbital coefficients according to
      CHECK(FI,FJ,Y,70)               abbreviated symmetry description.  Test whether
      £=xMOD(FI+FJ)                   sum or difference of suitable pairs is zero, if
      JUMP97,£≥Y                      so prepare symmetry species code in CQ, otherwise
      CQvGn+Gn                        go to 97) to punch asterisks.
      JUMP71
   70)CQv6                            repeat for sets of atoms Co, C1, (C2) and
   71)JUMP78,3.5≥G                    C3, C4, (C5) - select lower symmetry.
      I=xINTPT(B+C(S+2))
      620,27
      CHECK(FJ,FI,Y,73)
      £=xMOD(FJ+FI)
      JUMP97,£≥Y
      CQvCQ-Gn
      JUMP78
   73)CQvCQ+Gn
   78)JUMP77,S≥1
      Q=7
      S=3
      JUMP72
   77)JUMP75,C7≥C6
      C6=C7
   75)JUMP6,3.5≥G
      JUMP7,C6≥6
      JUMP5,C6≥4
      JUMP3,C6≥2

    1)620,1
      620,0
      620,1
      620,27
      620,21                          'A1U-A'
      620,0
      620,11
      620,27
      620,1
      JUMP91
    3)620,2
      620,0
      620,2
      620,27
      620,7                           'B2G-A'
      620,0
      620,11
      620,27
      620,1
      JUMP92
    5)620,2                                          } D2h labels
      620,0
      620,1
      620,27
      620,7                           'B1G-S'
      620,0
      620,11
      620,27
      620,19
```

```
91)620,25                'YA
620,1
JUMP94
7)620,2
620,0
620,19
620,27
620,21                   'B3U-S'        D2h labels
620,0
620,11
620,27
620,19
92)620,25                'YS'
620,19
94)620,26                'Z'
SPACE
JUMP98

6)620,14
620,14
620,27
JUMP2,3≥C6
JUMP80,2.5≥G
620,1
620,21
620,0                    'AU-S'
620,11
620,27
620,19
JUMP86
80)620,2
620,0
620,1                    'B1-S'         C2v and C2h labels
620,11
620,27
620,19
JUMP83
2)JUMP81,2.5≥G
620,2
620,7
620,0
620,11                   'BC-A'
620,27
620,1
JUMP86
81)620,1
620,0
620,2
620,11                   'A2-A'
620,27
620,1
83)620,26                'Z'
620,0
JUMP90
86)620,0                 'O'
620,16
90)620,14
620,14
JUMP98
97)SPACE
620,14
620,14
620,3
620,3
620,3
620,14
620,14                   'xxx'
620,14
O=N
98)REPEAT                change from 'selected atoms' to 'all atoms'
```

A77

```
59)JUMP87,O≠N
   J=I(I)N
58)NEWLINE
   PRINT(J)2,0                    print atom number
   I=KN+J
   Q=J(N)I
   PRINT(FQ)I,5                   print MO coefficients
   REPEAT
   JUMP89,O≠N
   REPEAT
   JUMP99
87)L=I(I)O
   J=XINTPT(V(L-I))               selected atom No.
   JUMP58
89)REPEAT
99)T=T+I                          count blocks of 6 columns
   R=R-6
   CvN+KN+C
   620,I3
   JUMP5I,R≥I                     return for next block.
79)ACROSS40/3 ──────────────►

   PSA
   CLOSE
```

Programme C

```
CHAPTER 2
VARIABLES 1

49) I=0(1)3 1
620,0
REPEAT
O=XINTPT(Fn)
DuZn-Fn
K=O-1
J=O+32 1
L=32(1)J
Q=XMIN(Uo,0,K)
ZL=UQ
UQ=1000
REPEAT
X7(D)Z32,0
JUMP79,0.4≥Un
R=XINTPT(H)
Q=R-1
K=XINTPT(XHn)
A=XFRPT(Un+Un)
S=0
JUMP44,Un≥0.7
S=1
JUMP47
44) Y=0.000001
JUMP50,1.7≥Un
620,30
620,13
620,13
620,27
620,5
620,14
620,5
620,18
620,7
620,25
620,0
620,13
620,14
620,27
620,19
620,0
620,10
620,16
JUMP47,A≥Y
I=0(1)8
620,14
REPEAT
620,27
620,19
620,0
620,10
620,16
620,28
620,2
620,21
47) VnuC-K-K
```

see FLOW CHART 2 (this version prints symmetry labels with the energy as well as with the coefficients)

punch 3 inches
blank tape

O = number of selected atoms

take selected atoms in Uo ...
and rearrange them in ascending numerical order in Z32 ... .

store rearranged list

R = number of orbitals to be tabulated

if S ≠ 0 orbital energies not to be tabulated

if only coefficients are wanted

'ENERGY
S=0'

'S = 0.25'

Vn = 1 if number of π-electrons is odd, 0 if even.

```
E=Fn
Z=Fn
T=-1
I=0(1)Q
JUMP45,S≠0
620,0
620,30
620,13
PRINT(I+1)2,0
PRINT(FI)1,7
45)£=Gn+XXFI
VI=FI/£
JUMP57,I≥K
E=E+FI
Z=Z+VI
57)JUMP46,S≠0
JUMP59,A≥Y
PRINT(VI)1,7
59)620,14
620,14
620,27
JUMP1,En≥ZI

JUMP80,2.5≥G
620,2
620,7
620,0
620,11
620,27
620,1
JUMP86
80)620,1
620,0
620,2
620,11
620,27
620,1
JUMP83
1)JUMP81,2.5≥G
620,1
620,21
620,0
620,11
620,27
620,19
86)620,0
620,16
JUMP98
81)620,2
620,0
620,1
620,11
620,27
620,19
83)620,26
98)JUMP60,T≠-1
46)REPEAT
```

print energy parameters m_j (EI)

accumulate total π-energy

if A = 0 print k_j (VI)

'BG-A'

'A2-A'

'AU-S'

'o'

'B1-S'

'Z'

print symmetry label

```
      JUMP 48, En≥Vn*
      F=F+XFK
      Z=Z+XVK
   48)620,0
      620,30
      620,13
      620,13
      620,27
      620,20
      620,15
      620,20
      620,1
      620,12
      SPACE
      620,27                    'TOTAL PI ENERGY'
      620,16
      620,9
      SPACE
      620,27
      620,5
      620,14
      620,5
      620,18
      620,7
      620,25
      NEWLINE
      PRINT(F+F)6,7
      JUMP62,A≥Y                print total π-energy
      PRINT(Z+Z)1,7
   62)JUMP79,2.7≥Un

   50)620,30
      620,13
      620,13
      620,27
      620,3
      620,15
      620,5
      620,6                     'COEFFICIENTS'
      620,6
      620,9
      620,3
      620,9
      620,5
      620,14
      620,20
      620,19
      620,0
      BvEn
      £v0
      JUMP66,62≥N
      J=0+31
   68)J=J-1                     if N >62 all coefficients for a block
      JUMP68,ZJ≥63               cannot be stored at once so the block
      0=J-31                     is split into two parts.
      J=62
      JUMP88
   66)J=N

   88)T=0                       T = counter for blocks of 6 columns
   51)620,30
      620,13
   55)JUMP53,5≥R
      K=6
      JUMP52
   53)K=R                       K = number of columns in a block
   52)JUMP73,62≥N
      K=K-1
```

```
      Q=KJ
   [  I=o(J)Q
   [  X6(B+F)VI,J
   [  BVN+B
      REPEAT
   [  JUMP74
      73)Q=NK
      K=K-1
      X6(B+F)Vo,Q
      BVQ+B
      74)620,14
      620,14
   [  L=o(1)K
   [  PRINT(6T+L+1)7,o        print orbital numbers as column headings
      REPEAT
      620,30
      620,13
      620,27
      620,5                   'E'
      SPACE
      620,14
      620,14
      620,14
   [  L=o(1)K
   [  I=6T+L
   [  PRINT(FI)1,5            print energy parameters m_j
      REPEAT
   [  JUMP61,N≥33
   [  620,30
   [  620,13
   [  620,14
   [  620,14
   [  620,14
   [  620,14
   [  L=o(1)K
   [  I=6T+L                  cycle for printing symmetry labels
   [  620,14
   [  JUMP59
      60)SPACE
      620,14
      REPEAT
      61)L=1(1)O
      S=XINTPT(Z(L+31))       selected atom No.
      620,30
      620,13
      620,30
      PRINT(S)2,o             print atom No.
      Q=KJ+S
   [  I=S(J)Q
   [  PRINT(V(I-1))1,5        print MO coefficients
   [  REPEAT
      REPEAT
      T=T+1                   count blocks
      R=R-6
      620,13
      JUMP51,R≥1
      R=R+6T
      K=O+32
      O=XINTPT(-O+£)
      JUMP79,o≥0
      S=O+31
   [  I=32(1)S
   [  ZI=ZK                   prepare to tabulate 'bottoms' of blocks if N > 62
   [  K=K+1
   [  REPEAT
      BV62
      J=N-62
      JUMP88

      79)ACROSS40/3 ──────────►

      PSA
      CLOSE
```

Programme D

see FLOW CHART 2 (this version prints symmetry labels with the energy as well as with the coefficients)

```
CHAPTER2
VARIABLES1

→49)I=0(1)30
  620,0                    punch 3 inches blank tape
 REPEAT

 0=XINTPT(Fn)              0 = number of selected atoms
 X6(D)£0,0                 selected atoms
 K=0-1
 J=32
┌L=0(1)K
│Q=XMIN(£0,0,K)           take selected atoms in £0 ...
│ZJ=£Q                    and rearrange in ascending
│J=J+1                    numerical order in Z32 ...
│£Q=1000
└REPEAT
 X7(D)Z32,0                store rearranged list
 U=XFRPT(Un)
┌JUMP67,U≥0.4
│R=XINTPT(NX+0.6)          R = number of orbitals to be tabulated
┌JUMP56
→67)R=N
→56)JUMP79,0.4≥Un
 Q=R-1
 K=XINTPT(CX)
 A=XFRPT(Un+Un)
 S=0
┌JUMP44,Un≥0.7             if S ≠ 0 orbital energies not to be tabulated
│S=1
│JUMP47
→44)Y=0.000001
┌JUMP50,1.7≥Un             if only coefficients wanted
│620,30
│620,13
│620,13
│620,27
│620,5
│620,14
│620,5
│620,18
│620,7
│620,25
│620,0                     'ENERGY
│620,13                           S = 0'
│620,14
│620,27
│620,19
│620,0
│620,10
│620,16
└JUMP47,A≥Y
 I=0(1)8                                  'S = 0.25'
 620,14
 REPEAT
 620,27
 620,19
 620,0
 620,10
 620,16
 620,28
 620,2
 620,21
→47)VnvC-K-K               Vn = 1 if number of π-electrons is odd
                                0 if even.
```

```
E=En
Z=En
T=-1
I=0(1)Q
  JUMP45,S≠0
  620,0
  620,30
  620,13
  PRINT(I+1)2,0
  PRINT(EI)1,7
45)£=Gn+XXEI
  VI=EI/£
  JUMP57,I≥K
  E=E+EI
  Z=Z+VI
57)JUMP46,S≠0
  JUMP59,A≥Y
  PRINT(VI)1,7
59)620,14
  620,14
  620,27
  JUMP1,En≥ZI
  JUMP3,Gn≥ZI
  JUMP2,2≥ZI

4)620,1
  620,0
  620,1
  620,27
  620,21
  620,0
  620,11
  620,27
  620,1
  JUMP91
3)620,2
  620,0
  620,2
  620,27
  620,7
  620,0
  620,11
  620,27
  620,1
  JUMP92
2)620,2
  620,0
  620,1
  620,27
  620,7
  620,0
  620,11
  620,27
  620,19
91)620,25
  620,1
  JUMP94
1)620,2
  620,0
  620,19
  620,27
  620,21
  620,0
  620,11
  620,27
  620,19
92)620,25
  620,19
94)620,26
  JUMP60,T≠-1
46)REPEAT
```

print energy parameters m_j (KI) and, if A = 0, k_j (VI)

'A1U-A'

'B2G-A'

'B1G-S'

'YA'

'B3U-S'

'YS'

'Z'

```
    JUMP48,En≥Vn*
    E=E+XEK
    Z=Z+XVK
48)620,0
   620,30
   620,13
   620,13
   620,27
   620,20
   620,15
   620,20
   620,1
   620,12
   SPACE
   620,27                    'TOTAL PI ENERGY'
   620,16
   620,9
   SPACE
   620,27
   620,5
   620,14
   620,5
   620,18
   620,7
   620,25
   NEWLINE
   PRINT(E+E)6,7
   JUMP62,A≥Y
   PRINT(Z+Z)1,7             print total π-energy
62)JUMP79,2.7≥Un

50)620,30
   620,13
   620,13
   620,27
   620,3
   620,15
   620,5
   620,6                     'COEFFICIENTS'
   620,6
   620,9
   620,3
   620,9
   620,5
   620,14
   620,20
   620,19
   620,0
   BvEn
   JUMP66,62≥N               if N >62 all coefficients for a block cannot
68)J=J-1                     be stored at once so block is split into
   JUMP68,ZJ≥63              two parts
   0=J-31
   J=62
   JUMP88
66)J=N

88)T=0                       T = counter for blocks of 6 columns
```

```
51)620,30
   620,13
55)JUMP53,5≥R
   K=6                                  K = number of columns in a block
   JUMP52
53)K=R
52)JUMP73,62≥N
   K=K-1
   Q=KJ
   I=0(J)Q
   X6(B+F)VI,J
   BvN+B
   REPEAT
   JUMP74
73)Q=NK
   K=K-1
   X6(B+F)V0,Q
   BvQ+B
74)620,14
   620,14
   L=0(1)K
   PRINT(6T+L+1)7,0                     print orbital Nos. to head columns
   REPEAT
   620,30
   620,13
   620,27
   620,5                                'E'
   SPACE
   620,14
   620,14
   620,14
   L=0(1)K
   I=6T+L
   PRINT(EI)1,5                         print energy parameters m_j
   REPEAT
   620,30
   620,13
   JUMP61,N≥33
   620,30
   620,14
   620,14
   620,14
   L=0(1)K
   I=6T+L                               cycle for printing symmetry labels
   JUMP59
60)620,0
   REPEAT
61)L=1(1)0
   S=XINTPT(Z(L+31))                    selected atom No.
   620,30
   620,13
   620,30
   PRINT(S)2,0                          print atom No.
   Q=KJ+S
   I=S(J)Q
   PRINT(V(I-1))1,5                     print MO coefficients
   REPEAT
   REPEAT
   T=T+1                                count blocks
   R=R-6
   620,13
   JUMP51,R≥1
   R=R+6T
   K=0+32
   0=XINTPT(-0+Fn)
   JUMP79,0≥0                           prepare to tabulate 'bottoms of blocks' if N>62
   S=0+31
   I=32(1)S
   ZI=ZK
   K=K+1
   REPEAT
   Bv62
   J=N-62
   JUMP88
```

```
79)I=28
X6(Yn)Eo,P
X6(Zn)Fo,P          take bond list
S=XINTPT(Hn)
HnvC
K=P-1
L=o(1)K
Q=XMIN(Eo,o,K)
JUMP65,Q≥S
ZIvL+Gn
I=I+1
65)AL=EQ
£L=FQ               place in order according
EQ=1000              to first atom of the bond.
REPEAT
I=I-28
X7(Yn)Ao,P
X7(Zn)£o,P          store re-ordered bond list
X7(V)Z28,I          store list of selected bonds
ACROSS40/3

PSA
CLOSE
```

CHAPTER3

see FLOW CHART 1

```
£→I
D→45
G→45
H→45
A→59
F→59
E→29
Y→28
B→40
Z→38
C→20
X→I3
U→45

40)CvHn
W=0.000001
K=XINTPT(XHn-W)
X6(NN+F)Hn,4
UnvWn+Vn
JUMP58,X≥Un
JUMP41,20≥£K
X6(Xn)£0,N
41)I=K+I
JUMP43,£(N-I)≥En
I=N
43)T=K
44)K=K+I
JUMP45,K≥I
£v£T-£K
JUMP44,W≥£
45)JUMP48,0≥T
T=T-I
£v£T-£(K-I)
JUMP45,W≥£
T=T+I
48)E=XDIVIDE(C-2T,K-T)
JUMP42,99≥Vn

620,30
YvT
620,13
620,13
620,30
620,27
620,3
620,8
620,I
620,18
620,7
620,5
SPACE
620,11
620,14
620,27
620,2
620,15
620,14
620,4
SPACE
620,27
620,15
620,18
620,4
620,5
620,18
SPACE
620,27
620,13
620,I
620,20
620,18
620,9
620,24
```

prepare constants: K, T, E for 'equalization' over degenerate orbitals.

This chapter calculates and tabulates charges, bond orders and free valences.

'CHARGE - BOND ORDER MATRIX'

```
620,0
620,30
Q=0(1)8
[ 620,14
[ REPEAT

S=0
J=N-1
An=En
JUMP13,Vn≥250
M=XINTPT(Fn)
DM=En
X6(D)Do,M
13)GvGn+Gn
I=0(1)344
[ GI=En
[ REPEAT
I=0
14)O=0
X6(NI+F)Xo,N
Q=0(1)5
L=S+Q
JUMP15,L≥N
JUMP18,Vn≥250
L=XINTPT(DL-X)
JUMP15,-1≥L
R=0
JUMP17
18)R=L
17)R=R(1)J
GO=GO+GXLXR
O=O+1
[ REPEAT
JUMP19
15)E=En
19)REPEAT
I=I+1
JUMP16,I≥K
JUMP14,I≠T
GvE
JUMP14
16)X7(An)Go,O
AnvO+An
S=S+6
JUMP13,E≥Gn
R=N
HvGn+Gn
JUMP12,250≥Vn
DOWN27/4
VnvEn
JUMP39
12)Vn=En
Un=-Gn
DOWN68/4

32)UnuWn
T=XINTPT(Y)
42)JUMP58,X≥Un
```

if Vn ⩾ 250 calculate and tabulate complete upper triangle of matrix by rows (= lower triangle by cols).

selected atoms.

I'th eigenvector of orbital coefficients.

add term to each of a column of quantities.

for partially occupied orbitals.

for triangular tabulation.

for rectangular tabulation.

```
X6(Yn)BI,P
X6(Zn)CI,P
R=o(I)P
DR=En
FR=En
REPEAT
J=N-I
I=o
GvGn+Gn
46)X6(NI+F)Ao,N
JUMP47,I.5≥Vn
R=o(I)J
DR=DR+GARAR
REPEAT
47)Q=I(I)P
L=XINTPT(BQ)
M=XINTPT(CQ)
FQ=FQ+GA(L-I)A(M-I)
REPEAT
I=I+I
JUMP33,I≥K
JUMP46,I≠T
GvE
JUMP46

33)JUMP35,X≥Wn
J=J(-I)o
AJ=I.732051
REPEAT
Q=I(I)P
L=XINTPT(BQ-X)
M=XINTPT(CQ-X)
AL=AL-FQ
AM=AM-FQ
REPEAT

35)620,30
620,I3
620,I3
JUMP50,X≥Vn
620,27
620,2
620,I5
620,I4
620,4
SPACE
620,27
620,I5
620,I8
620,4
620,5
620,I8
620,I9
SPACE
JUMP52,I,5≥Vn
I=I(I)I0
620,I4
REPEAT
620,27
620,3
620,8
620,I
620,I8
620,7
620,5
620,I9
```

bond list.

I'th eigenvector of orbital coefficients.

charges on all atoms.

for partially occupied orbitals.

compute free valences for all atoms.

'BOND ORDERS'

'CHARGES'

A90

```
    620,0
52) JUMP51, X≥Wn
    I=1(1)10
    620,14
    REPEAT
50) JUMP51, X≥Wn
    620,27
    620,6
    620,18
    620,5
    620,5
    SPACE
    620,27
    620,22
    620,1
    620,12
    620,5
    620,14
    620,3
    620,5
    620,19

51) NEW LINE
    θ=XINTPT(Fn)
    S=XINTPT(Hn)
    JUMP59, S=P
    X6(V)Ho,S
    X6(D)Yo,O
59) I=o
106) JUMP60, S≠P
    L=I+1
    M=I
    JUMP54
60) L=XINTPT(HI)
    M=XINTPT(YI-X)
54) 620,30
    620,13
    620,30
    JUMP53, X≥Vn
    JUMP56, I≥S
    PRINT(BL)2,0
    PRINT(CL)2,0
    PRINT(FL)1,5
57) JUMP53, 1.5≥Vn
    PRINT(M+1)4,0
    PRINT(DM)1,5
53) JUMP55, X≥Wn
    PRINT(M+1)4,0
    PRINT(AM)1,5
55) I=I+1
    JUMP106, O>I
    JUMP58, I≥S
    JUMP58, En≥Vn
    Vn=Gn
    Wn=En
    JUMP106

56) Q=o(1)19
    620,14
    REPEAT
    JUMP57

58) K=XINTPT(CX+1.2)
    ACROSS58/5 ——————→

    PSA
    CLOSE
```

'FREE VALENCES'

number of selected atoms.
number of selected bonds.

selected bonds.
selected atoms.

print bonded atom Nos.

print bond order.

print atom No.
print charge.

print atom No.
print free valence.

```
CHAPTER4

VARIABLES3

                    ┌──────────────
```

Common routine for calculating all polarizabilities

```
60) JUMP59,45≥S
    S=S-46
    E=S
    S=46
    JUMP58
59) E=En
58) S=S-1
    R=0(1)S
    READ(GR)
    READ(HR)
    DR=En
    REPEAT
62) C=En
63) I=0
    L=N-1
61) X6(IN+F)A0,N
    J=K(1)L
    X6(JN+F)F0,N
    U=XDIVIDE(G,E=-EI)
    R=0(1)S
    £vU
    Q=XINTPT(GR)
    CnvEn
    JUMP65,H≠Gn
64) T=XINTPT(BQ)
    Q=XINTPT(CQ)
    £=£A(Q-1)F(T-1)+£A(T-1)F(Q-1)
    JUMP66
65) £=2£A(Q-1)F(Q-1)
66) JUMP67,Cn≥Gn
    CnvGn
    Q=XINTPT(HR)
    JUMP64,1.5≥H
    JUMP65
67) DR=DR+£
    REPEAT
    REPEAT
    I=I+1
    JUMP61,K≠I
    JUMP24,Gn≥C

    R=S+1
    X7(An)D0,R
    AnvR+An
    JUMP101,Un≥En
    X6(Dn)D0,M
101) R=0
    JUMP117,Bn>An
    R=XINTPT(Z)
    JUMP127,En≥Un
    JUMP114,En≥H
```

pairs of atoms/bonds to be read from a data tape.

I'th eigenvector (occupied)

J'th eigenvector (unoccupied)

calculate the (i,j) term in the summation for all the S+1 pairs of GR, HR.

Meaning of H:
- 2 = atom-atom
- 1 = bond-bond
- -1 = atom-bond

add (i,j) term to accumulated sum.

store set of polarizabilities just computed.

jump for rectangular tabulation

```
27) Cn=En
28) JUMP104, H≥1.5
    S=271
    JUMP29
104) S=478
 29) VnvS+1
    JUMP30, An≥Vn
    S=XINTPT(An)
 30) X6(Cn)Do, S
    UvS
    JUMP32, Cn≥X
    T=0
 32) J=0
 22) Q=6T
    L=Q+1
    I=L+5
    JUMP26, R≥I
    I=R
 26) 620, 0
    620, 13
    S=L(1)I
    £v-Gn
    JUMP108
 33) JUMP36, £≥En
    REPEAT
 23) 620, 30
    620, 13
    J=J+1
    Q=Q+1
    O=L-1
    S=Q
    £vEn
    JUMP107
 36) M=J-1
 21) PRINT(DM)1, 5
    O=O+1
    JUMP20, O≥I
    JUMP20, O≥Q
    M=M+R-O
    JUMP21
 20) JUMP23, R≠Q
    JUMP24, O≥R
    T=T+1
    620, 30
    620, 13
    620, 30
    S=0(1)8
    620, 14
    REPEAT
    J=M+1
    A=36T-6R-J+U
    JUMP22, A≥-14.5
    CnvJ+Cn
    Anv-J+An
    JUMP28

124) S=XINTPT(D(Q-1))
    £vGn
108) JUMP109, H≠Gn
107) JUMP109, H≥1.5
    JUMP109, P≥46
    PRINT(BS)2, 0
    PRINT(.49-CS)2, 0
    JJMP121
```

S = number of elements which may be held in the working store at any one time.

T = counter for blocks tabulated

to print column headings

triangular tabulation

to print row heading

print a row of the matrix.

count blocks

prepare for next block

row or column headings:

atom numbers for bonds

```
127)W=En
   JUMP68,46≥M
   UnvX
   JUMP68
114)M=N

68)T=0                                  T = counter for blocks tabulated
   Cn=En
69)620,0
   620,13
   JUMP126,5≥M
   J=6
   JUMP125
126)J=M
125)O=JR
   L=1(1)J
   Q=6T+L
   JUMP124,En≥Un                        to print col headings if bonds or sel. atoms.
   PRINT(Q)5,0
   620,14
   620,14
120)REPEAT
   X6(Cn)Go,O                           set of quantities for tabulation
   L=1(1)R
   S=XINTPT(L+Vn)
   620,30
   620,13
   £vGn+Gn
   JUMP107
109)PRINT(S)5,0                         atom number as row heading
   620,14
   *620,14
121)JUMP33,X≥£                                                    rectangular
   JUMP120,Gn≥£                                                   tabulation
   I=L+O-R
   Q=L(R)I
   PRINT(G(Q-1))1,5                     print one row of the matrix
   REPEAT
   REPEAT
   T=T+1
   M=M-6
   CnvTO
   JUMP105,M≥1
   JUMP24,X≥W
105)620,30
   620,13
   620,30
   S=0(1)8
   620,14
   REPEAT
   JUMP69,M≥1
   Vn=Z
   ZvW
   W=En
   M=XINTPT(Fn)
   JUMP123

24)UP                                   return to main programme

   PSA
   CLOSE
```

```
CHAPTER5

VARIABLES3

58)Wn vXn
£0vYn
£1vZn
X6(NN+F+4)Xn,3
£=Xn+Yn+Zn
JUMP70,X≥£
X6(Wn)E0,N
K=K-1
NEWLINE
620,13
620,27
620,16
620,15
620,12
620,1
620,18
620,9
620,26
620,1
620,2
620,9
620,12
620,9
620,20
620,9
620,5
620,19

JUMP80,X≥Xn
NEWLINE
620,13
620,27
620,1
620,20
620,15
620,13
620,0
620,11

620;27
620;17
620,20
620,15
620,13
HvGn+Gn
G=Gn
DnvD
M=XINTPT(Fn)
JUMP71,195≥Xn
ZvN
JUMP122,250≥Xn
DOWN111/4
JUMP80
122)DOWN110/4
JUMP80

71)Wv-Gn
JUMP72,92≥Xn
EvXn-100
0=N
```

see FLOW CHART 1

Control chapter for polarizability calculations.

'POLARIZABILITIES'

'ATOM-ATOM'

to compute and tabulate matrix of π_{AA}

```
          84)Vn=Gn
          JUMP74,M≠0
          JUMP85,46≥0
          Q=0-47
          S=45
          VvQ
          JUMP75
74)X6(Dn)Go,M
85)S=M-1
75)R=o(1)S
          JUMP87,M≠0
          GRvR+Vn
87)HR=GR
          DR=En
          REPEAT
          DOWN62/*4 ------------------>
          JUMP83,Gn≥H

73)R=o(1)S
          NEWLINE
          PRINT(GR)2,0
          PRINT(HR)2,0
          PRINT(DR)1,5
          REPEAT
          JUMP86,W≥En
          XnvE
72)JUMP80,X≥Xn
          S=XINTPT(Xn)
          DOWN60/4 ------------------>
          JUMP73

80)JUMP92,X≥Yn
          NEWLINE
          620,13
          620,27
          620,2
          620,15
          620,14
          620,4
          620,0
          620,11
          620,27
          620,2
          620,15
          620,14
          620,4
          HvGn
          G=Gn+Gn
          DnvV
          M=XINTPT(Hn)
125)X6(Wn)Eo,N
          X6(£o)B1,P
          X6(£1)C1,P
          JUMP126,En≥H
          JUMP81,195≥Yn
          ZvP
          JUMP123,250≥Yn
          DOWN111/4 ------------------>
          JUMP90
123)DOWN110/4 ------------------>
          JUMP90

81)Wv-Gn
          JUMP82,92≥Yn
          EvYn-100
          0=P
          JUMP84
```

list of atoms/bonds for self polarizabilities

to compute

tabulate column of π_{AA}

'BOND-BOND'

recover energy parameters (overwritten during tabulation)

bond list

to compute and tabulate matrix of π_{BB}

```
A97
        96)YnvE
        82)JUMP90,X≥Yn
          S=XINTPT(Yn)
          DOWN60/4 ──────────────────────→ to read list of pairs of bonds and
                                           compute
        83)R=0(1)S
          NEWLINE
          L=XINTPT(GR)
          T=XINTPT(HR)
          PRINT(BL)2,0
          620,11
          PRINT(CL)2,0
          620,15                          tabulate column of π_BB
          PRINT(BT)2,0
          620,11
          PRINT(CT)2,0
          PRINT(DR)1,5
          REPEAT
        JUMP96,-0.5≥W
      →86)Vnv47
        S=Q
        Wv-Gn
        JUMP75


      →92)Bnv300
      →90)JUMP70,X≥Zn
        NEWLINE
        620,13
        620,27
        620,1
        620,20
        620,15
        620,13                            'ATOM-BOND'
        620,0
        620,11
        620,27
        620,2
        620,15
        620,14
        620,4
        Hv-Gn
        G=Gn+Gn
      JUMP125,Bn≥272
    →126)JUMP91,195≥Zn
        ZvP
      JUMP124,250≥Zn
        YvN
        DOWN113/4 ──────────────────→
      JUMP70                                }
    →124)M=XINTPT(Fn)                       } to compute and tabulate matrix of π_AB
        DnvD                                }
        DOWN110/4 ──────────────────→


    →70)ACROSS10/0 ──────────────────→ return to start of programme for next
                                       molecule.

    →91)S=XINTPT(Zn)
      DOWN60/4 ──────────────────→ to read list of atom-bond pairs and
                                   compute
      R=0(1)S
      NEWLINE
      T=XINTPT(HR)
      PRINT(GR)2,0
      620,15
      PRINT(BT)2,0
      620,11                            tabulate column of π_AB
      PRINT(CT)2,0
      PRINT(DR)1,5
      REPEAT
    JUMP70,X≥E
      ZnvE
    JUMP91


      PSA
      CLOSE
```

```
PROGRAMME-517
CHAPTER1
A→119
B→119
C→119
D→119

1)T=-2
JUMP50
2)T=-1
JUMP50
3)T=0
50)S=N-1
£vN
A=1
B=0
C=2
JUMP19,2≥N

J=2(1)S
Q=J-1
VvQ
X6(V£-£+An)Ao,N
DnV££-V£+An
P=N-J
X6(Dn)Do,P
I=0
Y=0.000000000 00000006
Y=YY
K=J(1)S
CHECK(AK,B,Y,12)
Z=XRADIUS(AK,AQ)
W=A/Z
DI=WAK
AK=WAQ
AQ=Z
JUMP13
12)AK=A
DI=B
13)I=I+1
REPEAT
X7(V£-£+An)Ao,N
X7(Dn)Do,P
DnvV£+An
En£+Dn
X6(Dn)Bo,N

K=J(1)S
P=N-K
X6(K+En)CK,P
I=K-J
Y=CAKBKDI
X=AKAK
W=DIDI
Z=WCK+XBQ+Y
BK=XBK-WBK+AKCKDI-AKBQDI
CK=XCK+WBQ-Y
BQ=Z
P=K+1
JUMP18,P≥N
16)(CP,BP)=(CP,BP)*(AK,DI)
P=P+1
JUMP16,P≠N
P=K+1
17)I=I+1
(CP,BK)=(CP,BK)*(AP,DI)
P=P+1
JUMP17,P≠N
18)P=N-K
X7(K+En)CK,P
En£+En
REPEAT

X7(Dn)Bo,N
REPEAT
```

Given a real symmetric matrix A this programme uses Givens' method to reduce it to codiagonal form C and finds the eigenvalues λ_i and eigenvectors x_i which are such that $Ax_i = \lambda_i x_i$.

Entry 1) - All eigenvalues

Entry 2) - All eigenvalues and vectors

Entry 3) - Convert A to C only

N = order of the matrix

Constants throughout the programme

If no codiagonalization required

Replace matrix A stored in N^2 locations starting at An (lower triangle is not used so need not be set up) by its codiagonal form C = T'AT where T is an orthogonal matrix of 'sines and cosines' stored in place of the rest of A.

CODIAGONALIZATION

```
19)JUMP 55,T≥0
   ACROSS 51/2

8)T=0
  JUMP 20
4)T=2
  JUMP 20
5)T=1
20)ACROSS 20/2
7)ACROSS 7/2

55)UP ——————————→

  PSA
  XSQRT
  PSA
  CLOSE


  CHAPTER 2
  VARIABLES 1

51)Envc n-N
  P=1
  I=1(1)N
  JUMP 20
52)Bnv A+Bn
  JUMP 54,-2≥T
  Cnv£+Cn
54)REPEAT
  JUMP 55

20)£vN
  M=0(1)S
  VvM
  X6(£V+V+An)C0,2
  AM=C0
  BM=C1
  REPEAT
  JUMP 30,T=0

  Z=A0
  JUMP 44,1≥N
```

Entry 8) Compute eigenvector for given eigenvalue Z

Entry 4) Compute I'th eigenvalue.

Entry 5) Compute I'th eigenvalue and eigenvector.

Entry 7) Orthogonalize I vectors stored in NI locations ending at Cn-1, eigenvalues ending at Bn-1.

The two chapters may be combined into one if the programme is to be run on Atlas.

Control cycle for computation of eigenvalues and eigenvectors.

Transfer codiagonal form into working store. Diagonal elements into Ao... , superdiagonal elements into Bo ... .

If N = 1, eigenvalue = matrix.

A100

```
        ZvB
        J=0
        K)=40)
        JUMP29
40)     JUMP43,Q≥I
        I=1-I
        Zv-A
22)     ZvCZ
        K)=41)
        JUMP29
41)     JUMP22,Q≥I
49)     JUMP23;J≥61
        Zvo.5Z
        J=J+1
        K)=48)
        JUMP29
48)     JUMP49,I>Q
        J=J-30
        JUMP21,J≥0
        J=1
21)     Y=Z
        J=J(1)30
        Yvo.5Y
        ZvZ+Y
        K)=42)
        JUMP29
42)     JUMP24,Q≥I
        ZvZ-Y
24)     REPEAT
23)     JUMP45,I≥1
        I=1-I
        JUMP45

43)     ZvA
        JUMP22

29)     Q=0
        X=A
        W=Z-Ao
        JUMP26,W≥B
        Q=Q+1
26)     M=1(1)S
        V=WZ-WAM-XB(M-1)B(M-1)
        CHECK(W,B,1000000000,25)
        V=0.0000000001V
        W=0.0000000001W
25)     X=W
        W=V
        JUMP36,V≥B
        JUMP37,X≥B
        JUMP28
36)     JUMP28,X≥B
37)     Q=Q+1
28)     REPEAT
        JUMP27,I≥1
        Q=-Q
27)     JUMP(K)

45)     JUMP44,1≥I
        Y=0.00000001
        W=XMOD(Z)
        JUMP46,A≥W
        Y=YW
46)     CHECK(D(I-2),Z,Y,47)
        JUMP44
47)     ZvD(I-2)-Y
44)     D(I-1)=Z
        X7(Bn)Z,1
        XvTT
        JUMP30,C≥X
        JUMP52,-1≥T
        JUMP55
```

Z = trial value of root.

Search ascending powers of 2

Search descending powers of 2

Find 30 significant binary places

Compute Sturm sequence of principal minors of C-λI, noting number of changes of sign.

Protection against excessively large numbers.

Compare signs of succeeding terms of sequence

±Q = number of sign changes
= number of roots greater than current Z

If root is equal to previous one subtract a suitable small quantity from it.

Store eigenvalue in auxiliary store at Bn.

COMPUTATION OF EIGENVALUES

A101

```
30)JUMP39,1≥N
   BS=B
   W=Ao-Z
   X=Bo
   Q=1(1)S
   M=Q-1
   Y=XMOD(W)                    Solve (C -λiI)Yi = bi  by
   V=XMOD(BM)                   Gauss elimination with interchanges.
   JUMP32,Y≥V
   Y=W/BM
   W=YZ-YAQ+X
   X=-YBQ
   AM=BM
   BM=AQ-Z                      interchange
   CM=BQ
   JUMP33
32)JUMP38,Y≥o.oooooooooooooooooo1
   W=o.oooooooooo oooooooo01
38)Y=BM/W
   AM=W
   BM=X
   W=AQ-XY-Z                    don't interchange
   X=BQ
   CM=B
33)REPEAT

   Q=S-1
   CQ=B
   Y=XMOD(W)
   JUMP34,o.oooooooooo oooooooo01≥Y
   AS=A/W                                   compute yn
   JUMP35
34)AS=1oooooooooo oooooooooo
35)M=Q(-1)o
   AM=XDIVIDE(A-BMA(M+1)-CMA(M+2),AM)       compute other
   REPEAT                                   components of
   JUMP39,2≥N                               y by back substitution

   J=N-3
   J=J(-1)o
   X6(J£+An)Bo,N
   X6(££-J£-£+An)Co,N           Convert the vector y to x by carrying
   Q=N-J-3                      out the inverse of the original
   M=N                          orthogonal transformation, using the
   K=J+1                        stored 'sines and cosines'.
   Q=Q(-1)o
   M=M-1
   (AK,AM)=(AK,AM)*(BM,CQ)
   REPEAT
   REPEAT

39)Y=B
   Q=o(1)S
   Y=AQAQ+Y
   REPEAT
   Y=XSQRT(A/Y)                 Normalize the vector x.
   Q=o(1)S
   AQ=YAQ
   REPEAT

   JUMP95,T≥o                   If finding only one vector
   JUMP91                       To orthonormalize if necessary.
```

COMPUTATION OF EIGENVECTORS

A102

```
7)JUMP55,1≥I
X6(Bn-I)Do,I
T=3
£vN
EnvCn-I£-£
P=1
K=I
I=2(1)K
CnvEn+I£
X6(Cn)Ao,N
JUMP91
90)REPEAT
JUMP55

91)J=P
92)JUMP95,J≥I
X6(En+J£)Bo,N
Y=B
Q=o(1)S
Y=AQBQ+Y
REPEAT
X=XMOD(Y)
JUMP93;X≥o.oooooo1
X=D(P-1)-D(I-1)
Y=o.oooooo1
W=XMOD(D(I-1))
JUMP96,A≥W
Y=YW
96)JUMP94,Y≥X
P=P+1
JUMP94
93)Q=o(1)S
AQ=AQ-YBQ
REPEAT
Y=B
Q=o(1)S
Y=AQAQ+Y
REPEAT
Y=XSQRT(A/Y)
Q=o(1)S
AQ=YAQ
REPEAT
94)J=J+1
JUMP92

95)X7(Cn)Ao,N
JUMP52,-1≥T
JUMP90,T≥3

55)UP

PSA
XSQRT
PSA
CLOSE
```

Recover the eigenvalues

Read vector from the auxiliary store

P = index of last vector known to be orthogonal to all previous vectors

Compute scalar product of present vector with previous vector

If non-orthogonal

If degenerate do not increase P

Subtract projection

Renormalize

Store orthonormalized vector

Return to main programme.

ORTHONORMALIZATION

APPENDIX A TO CHAPTER III

The following pages are teleprinter print-outs of the D_{2h} version of the programme for the Longuet-Higgins/Murrell method described in section III.3. This version rather than the C_{2v} one is given as it involves more elaborate facilities for making use of symmetry, etc., to reduce the amount of computation necessary. The print-outs should be read in conjunction with Flow charts III.3 and III.4. The conventions as to notes, etc., are the same as those in Appendix B to Chapter I, except that, as much of the programme is in machine language the explanations are in general somewhat fuller. It is not, however, expected that a reader without knowledge of the order code will be able to follow the programme in detail.

A104

```
TITLE
LONGUET-HIGGINS/MURRELL METHOD FOR JOINING HYDROCARBONS  - POOLE
TITLE
D2H - CONFIGURATION INTERACTION - SINGLY EXCITED CONFIGS.  - MI24

CHAPTER0
VARIABLES1                          see FLOW CHART III.3

 JUMP10

9)400(Yn)
 410,62
 400(Zn)
 410,60
 READ(N)
 M=0+1
 X6(-2180)F0,M
 X6(-2496)U0,48
 X6(-2448)C0,P
 JUMP33

10)HALT
 300,0
12)627,0
11)600,32
 200,32
 370,31
 290(11)
 370,29
 280(12)
 610,32
 200,32
 350,32
 280(9)

 READ(S)                            S = number of atoms in L fragment
 200(S)
 340,1
 210(M)                             number of pairs of atoms -1

 H=1
 102,0
 010(P)
 010(0)
 010(T)

1)READ(I)                           I = no. of atom above Oz
 READ(J)                            J = no. of atom below Oz
 READ(K)                            K = z-coordinate
 READ(L)                            L = y-coordinate
 JUMP22,K=0
 M=M-1                              reduce number of pairs by 1 if atom is not on Oy
22)200(P)                           (giving number of sets related by symmetry)
 270(K)
 290(29)                            note maximum z-coordinate in P
 P=K
29)200(0)
 270(L)
 290(25)                            note maximum y-coordinate in Q
 0=L
25)200(L)
21)330,3                                                        'GEOMETRY'
 290(21)
 320,1
 280(23)                            place '1' in sign digit of atom nos. of starred set
 J=J+512                            take codeword
23)400,58

 200(T)
 280(2)                             jump if R fragment being considered
 412(U0)                            store codeword in U0 ...
 072(M)
 182(1)                             repeat for next set of atoms
```

```
S=M+1                    S = number of sets of atoms related by symmetry
400,60
410(£)                   Preserve MNOP

READ(K)                  number of orbitals
Q=K-1
I=0
102,0
L=0                      address relative to Co of first orbital coefficient
P=0
O=M                      number of coefficients in an orbital
3)READ(J*)               nos. of orbitals of L fragment
400,58
412(Fo)                  store orbital codeword
L=L+S                    address of next orbital
072(Q)
182(3)                   repeat
4)032(K)
5)600,32                 search for 'letter shift'
200,32
370,27
280(5)
300,0                    clear sac for symmetry code no.
077(J)                   jump if J negative
090(37)                    (i.e. orbital is of R)
105,25                   B5 set to tape value of 'Y'
590(6)
8)004,32                 preserve previous character
6)600,32                 read character
075,32                   compare character with B5
080(8)
174,1
080(26)                  see if previous character was 'A'
324,0                    add 1 to symmetry code no.
26)175,25
080(7)                   jump if not seeking 'Y'
327,0                    double code no.
37)105,26                set B5 to tape value of 'Z'
590(6)
7)402(Fo)
717,0                    insert code no. into codeword
412(Fo)
072(Q)
182(5)                   repeat                                  'orbitals'
032(K)

I=o(1)O
R=I+P
14)READ(Z)               read orbital coefficient
450(1)
490(14)                  jump back if ≥ 1, i.e. was atom No.
CR=HZ                    store modified coefficient
R=R+O+1
072(Q)
182(14)                  repeat for next column
032(K)
REPEAT                   repeat for next row
I=o
022(K)
400,58
410(Gn)                  preserve LJKL
```

read symmetry label and insert correct symmetry code number into orbital codeword

```
→17)READ(T)
  JUMP18,T≥0
  Q=Q-T
  302,-1
  004(J)
→19)105,1
  124,1
  407(Fo)
  410,32
  014,32+
  400,32
  765,0
  715,0
  412(Fo)
  330,1
  072(Q)
  182(19)
  JUMP17
→18)JUMP15,T≥101
  JUMP16,-1≥J
  012(R)
  400(£)
  410,60
  Hv0.707106778
  106,0
→30)406(Uo)
  410,32
  200,33
  280(32)
  306,0
→31)407(Co)
  500(H)
  417(Co)
  220(S)
  270(L)
  290(32)
  590(31)
→32)076(M)
  186(30)

  200(T)
  340,0
  210(T)
  330,1
  210(N)
  102,0
  JUMP1

→2)412(Vo)
  072(N)
  182(1)

  200(O)
  327,0
  210(I)
  200(P)
  327,0
  210(K)
  340,-1
  210(L)
  400,58
  410(Un)
  AvIL+L
  JUMP27,164≥A
  NEWLINE
```

read next number from data

if negative - complementary codewords must be synthesized
no. of last orbital

no. of next orbital
codeword of stored orbital

insert orbital no.

change symmetry about Oz
store new codeword

repeat

if T > 100 further orbitals of the same fragment are expected
if J < 0 all orbitals have been read, since last one was of R.
restore MNOP for geometry of R

modifying multiplier for coefficients of R orbitals and for atoms on the y-axis in L orbitals

multiply orbital coefficients for atoms on y-axis by √2

number of pairs of atoms in an R fragment

to read the geometry of R

store geometry codeword of R

repeat

calculate size of γ-matrix that will need to be calculated
I = Max Δy
K = Max Δz
L = number of elements in a row

```
620,27
620,20
620,15
620,15
SPACE
620,27
620,2
620,9
620,7
NEWLINE
JUMP10

27)400(Gn)
410,58
P=L
READ(K)
Q=Q+K
002(R)
O=N
20)READ(J)
J=J+512
400,58
412(Fo)
L=L+T
072(Q)
182(20)
590(4)

15)K=T-100
Q=Q+K
JUMP3,J≥0
JUMP20

16)P=N+1
N=T
T=P
O=Q
P=L
33)010(R)
010(Q)
010,50
010,50+
010,51
010,51+
M=1(1)N
300,0
102,-2
34)600,32
006,32
176,18
080(35)
332,0
590(36)
35)176,12
080(34)
36)122,1
080(34)
312,0
012(I)
READ(J)
READ(K)
READ(E)
010(L)
103,0
```

if too big punches 'TOO BIG'

start next molecule

restore LJKL for orbitals of R

number of orbitals of R

orbital nos. of R
make negative to distinguish from those of L

store orbital codeword
address of next orbital

repeat
to read symmetry labels and coefficients

to read more orbitals of same fragment

N = number of configurations given in data

the 4 parts of register 50 are used to note
how many configurations there are of each of
the four possible symmetries.

read 'configuration type'

(L→L, L→R, R→L or R→R
I = 0, 1, 2 or 3)

'CONFIGURATIONS'

no. of vacated orbital
no. of acceptor orbital
diagonal matrix element

```
105,-2
172,2
090(45)
41)152,1
080(46)
42)403(Fo)
410,32
006,33+
200,32+
270(J)
280(43)
016,34+
707,0
327,0
327,0
590(44)
45)J=J+512
JUMP41
46)K=K+512
JUMP42

43)270(K)
280(39)
016,35
707,0
44)125,1

220(L)
210(L)
39)175,0
183(42)
340,0
340,0
260(L)
350,3
315,0
006(Q)
200,34+
210(J)
200,35
210(K)
*111,1
590(64)
111,3
002(I)
172,2
090(60)
111,2
152,1
080(61)
002(I)
111,2
172,3
090(60)
016(Q)
JUMP48

60)103,8
590(62)
61)103,2
62)063(L)
013(L)
165,2
64)400,58
416(Ho)
```

replace orbital nos. by the addresses of their first coefficients relative to Co ...

multiply symmetry code no. of vacated orbital by 4.

add symm. of acceptor to 4 x symm. of vacated

return if both orbitals not yet converted

compute configuration symmetry

change y-symmetry of vacated orbital

change y-symmetry of acceptor orbital

change y-symmetry of configuration

store configuration codeword

A109

```
400(E)
416(Eo)
205,50
314,0
404(Do)
410,36
306,0
215,36
400,36
414(Do)
304,1
215,50
126,1
074(R)
090(63)
591,0
63)014(R)
591,0

48)REPEAT

400,50
410(Gn)
400,60
410(Zn)
400,62
410(Yn)
PRESERVE

READ(H)
READ(J)
102,0
50)072(S)
090(52)
402(Uo)
707,0
077(J)
182(50)
132,1
012(J)
READ(K)
102,0
51)072(T)
090(52)
402(Vo)
707,0
077(K)
182(51)
132,1
012(K)
400,58
410(Vn)
ACROSS1/1
52)NEWLINE
620,27
620,14
620,15
SPACE
620,27
620,19
620,21
620,3
620,8
SPACE
620,27
620,1
620,20
620,15
620,13
NEWLINE
JUMP10

PSA
CLOSE
```

store diagonal matrix element

store config.no. in part of Do ... corresp. to present symmetry.
add 1 to number of configs. of present symm.

R = max number of configs in any one symm.

store codeword giving numbers of configs. of each type

preserve MNOP

preserve QRST

⌀ for join bond
atom in top half of L at join

replace atom no. with position in atom list
atom in top half of R at join

'JOIN DATA'

replace atom no. with position in atom list

error message:

'NO SUCH ATOM'

```
CHAPTERI
A→63
U→I5
V→3I
C→I23
B→I43
F→23
E→3I
H→3I
D→II

I)6Io,32
300,I28
250,32
280(9)
400,60
4Io(£)
400(Zn)
4Io,60
NEWLINE
PRINT(S)3,o
PRINT(T)3,o
PRINT(Q)3,o
PRINT(R)3,o
PRINT(O)3,o
PRINT(P)3,o
C=P-o.5
£M=O
O=64
P=S+63
N=R
S=Q
R)=2)
JUMP90
2)O=8o
P=T+79
R)=3)
JUMP90
3)O=380
P=M+380
R)=4)
JUMP90
4)NEWLINE
P=XINTPT(C)
Q=o(I)P
NEWLINE
PRINT(CQ)I,5
REPEAT
O=436
P=S+435
R)=5)
JUMP90
5)NEWLINE
M=S-I
L=o(I)M
NEWLINE
PRINT(EL)I,5
REPEAT
400(Gn)
4Io,58
NEWLINE
PRINT(I)3,o
PRINT(J)3,o
PRINT(K)3,o
PRINT(L)3,o
O=468
P=N+468
R)=6)
JUMP90
```

see FLOW CHART III.4

jump if handswitch 7 set

preserve MNOP

restore old MNOP

number of atom sets of L
number of atom sets of R
total number of configurations
largest number of configs of 1 symm. -1
total number of orbitals -1
total number of orbital coefficients

geometry codewords of L

geometry codewords of R

orbital codewords

orbital coefficients

configuration codewords

diagonal matrix elements

number of SySz configurations
number of SyAz configurations
number of AySz configurations
number of AyAz configurations

lists of configuration numbers in the 4 symmetries

print-out codewords, etc., to check data was correct and has been correctly converted by the programme

(this may be suppressed by putting up handswitch 7)

```
A\\\
                    →6)400(Vn)
                      410,58
                      NEWLINE
                      NEWLINE
                      PRINT(J)3,0
                      PRINT(K)3,0                    join atoms
                      PRINT(H)1,3                    join 'β'
                      400(£)
                      410,60
                      400(Yn)
                      410,62
                      JUMP9
                    →91)PRINT(O)3,0
                      PRINT(Q)3,0                    error print in case of mistake in chapter 0
                      620,31
                      620,31
                      620,31
                      JUMP(R)
                    →90)NEWLINE
                      JUMP91,O>P
                      Q=O(1)P                        subroutine for printing codewords
                      NEWLINE
                      400(AQ)
                      410,58
                      PRINT(I)3,0
                      PRINT(J)3,0
                      PRINT(K)3,0
                      PRINT(L)3,0
                      REPEAT
                      JUMP(R)
                    →9)400(Un)                       codeword with dimensions of γ-matrix
                      410,58
                      J=0
                      R=0(1)I                        rows of γ-matrix
                      Q=0(2)K                        columns of γ-matrix
                      200(Q)
                      006(R)
                      156,1
                      326,0
                      210,57+
                      400,56
                      520,56
                      520(3)
                      410,32
                      200(R)
                      210,57+
                      400,56
                      520,56
                      420,32
                      410(Z)
                      Z=XSQRT(0.4830252)             Z = actual distance in Å between atoms separated
                      JUMP73,5.52≥Z                    by R units in y-direction and Q in z-direction
                      400,32                         if Z ≥5.52 Å use reciprocal approximation: γ=14.42/Z eV
                      500(14.4)
                      590(74)
                    →73)400(0.2157)
                      500(Z)
                      430(2.625)
                      500(Z)                         if Z<5.52Å use parabola approximation:
                      420(10.53)                                γ= 10.53 ± 2.657Z + 0.2157Z²
                    →74)001(J)
                      411(Bo)                        store γ
                      121,1
                      011(J)
                      REPEAT
                      REPEAT
                      400,58
                      410(Un)                        store γ-matrix codeword
                      X7(3840)Bo,J
```

control cycle for configuration interaction calculation.
for the four symmetries

```
P=0(1)3
400(Gn)
410,50
006(P)
206,50
316,0
136,1
016(M)
006(P)
080(20)
320,1
20)210(N)

NEWLINE
620,13
620,13
620,30
PRINT(N)3,0
620,27
200(P)
370,2
290(21)
620,19
590(22)
21)620,1
22)620,25
350,1
280(23)
620,19
590(24)
23)620,1
24)620,26
SPACE
620,27
620,3
620,15
620,14
620,6
620,9
620,7
620,21
620,18
620,1
620,20
620,9
620,15
620,14
JUMP27,N≠1
200(P)
280(28)
NEWLINE
620,13
PRINT(0)5,0
620,27
620,3
620,13
620,0
620,11
620,1
620,13
620,30
620,13
JUMP26
27)620,19
28)NEWLINE
JUMP26,0≥N
DOWN104/2 ──→
```

M+1 = number of configs

N = number of configs

number of configs.

print symmetry label

'CONFIGURATION'

if only one config print zero eigenvalue if it is ground state - otherwise jump to next symmetry.

's'

for solution of configuration interaction problem for this symmetry.

```
400(Yn)

4I0,62
400(Zn)
4I0,58
400,3I.58
300,-63                    clear space for next matrix
25)4I70(A63)
380(25)
X6(-2496)Uo,48             recover geometry codewords
X6(-2156)Eo,64             recover diagonal matrix elements and config. codewords
X6(-2448)Co,L              recover orbital coefficients
400(Un)
4I0,58
X6(3840)Bo,J               recover matrix of γ's
26)REPEAT

ACROSSI0/0 ──────►

XSQRT
PSA
CLOSE
```

```
CHAPTER2                    see FLOW CHART III.4
VARIABLES1
```

```
→104)Anv0
  R=0
—I=0(1)M                    rows of configuration interaction matrix
  R=R+I
—J=I(1)M                    columns of configuration interaction matrix

  400,60
  410(V)
  010(M)

  400(DI)                   nos. of I'th configs of the 4 symmetries
  410,36
  006(P)                    extract no. of I'th config of P'th symm.
  206,36
  017(K)                    configuration codeword for this config.
  407(Ho)
  410,34
  400(DJ)                   similarly for J'th
  410,36
  006(P)
  206,36
  407(Ho)
  200,34
  327,0
  327,0
  727,-8
  210(Q)
┌090(118)
└360,-1
→118)320,1                  compute matrix element type
  620,30
  620,13
  627,0                     punch code character
┌119)597(119)               jump to appropriate calculation subroutine
→590(122)
→590(126)
→590(125)
→590(121)
→590(123)
→590(122)
→590(121)
→590(120)
  127)PRINT(AR)3,6          print matrix element just calculated
  R=R+1
—REPEAT                     repeat for elements in a row
  NEWLINE

—JUMP94,P≠0                 if symmetry is SySz compute matrix element
  400(DI)                    with ground state
  410,36
  006(P)
  206,36
  407(Ho)
  410,34
  400,31.58
  200,34
  370,2
┌280(91)
  004,35
  005,34+
└590(92)                    matrix element is 0 if type is 1 or 2
→91)370,1
┌280(93)
  004,34+
  005,35
→92)400(Vn)
  410,32
  024,32+
  025,33
```

```
A115  400(H)
      500(5.65685424)
      504(Co)
      505(Co)
      matrix element = 4 2c_r c_t β if type is 1 or 2
   93)410(AR)
      PRINT(AR)4,6
      NEWLINE
      R=R+1

   94)JUMP124,8≥N        if N>8 store matrix one row at a time
      R=0
      X7(An)Ao,N
      Anv N+An
   124)REPEAT

      JUMP102,N≥9
      X7(An)Ao,64        if N≤8 store complete matrix at one go
      JUMP103
   102)JUMP103,P≠0
      A(N-1)=0           final element for SySz (diagonal element for
      X7(An)Ao,N                                 ground state)

   103)Anv o
      Bnv NN             addresses for Programme -517
      0=P
      DOWN1/1-517 ------>  compute all eigenvalues of CI matrix
      Uv N
      Bnv Bn-U
      620,30
      620,13
      620,13
      620,30
      620,27
      620,5
      620,9
      620,7              'EIGENVALUES'
      620,5
      620,14
      620,22
      620,1
      620,12
      620,21
      620,5
      620,19
      NEWLINE
      X8(Bn,1,U,1,6)     print column of eigenvalues in eV
      Cnv Bn+1
      I=%N
      DOWN5/1-5117 ------>  find lowest eigenvalue and eigenvector
      P=0
      0=N+1
      X6(Bn)Ao,0
      NEWLINE
      620,27
      620,12
      620,15             'LOWEST'
      620,23
      620,5

      620,19
      62%0,20
      NEWLINE
      620,13
      PRINT(8067.5Ao)5,0   print lowest eigenvalue in cm^-1
      620,27
      620,3
      620,13
      620,0
      620,11
      620,1
      NEWLINE

   I=1(1)N
   NEWLINE
   PRINT(AI)1,4          print eigenvector coefficients
   REPEAT

                         return for next matrix
   UP ------>
```

```
      I26)AR=0                    matrix elements of type 6 (and others which are
      JUMPI27                                  zero because of symmetry)

      I21)4I0,36                  matrix elements of type 1          β- type elements
          200,36+                                                    between a
          270,34+                                                    locally excited
      280(I26)                    vacated orbitals not same          configuration
          200,35+                                                    and a transfer
          260,37+                                                    from it
          350,3
      280(I26)                    acceptors have opposite symmetry
          200(Q)
          350,I
      280(II0)
          004,37
          005,35
      590(III)
      II0)004,35                  set up addresses for coefficients for join atoms
          005,37
      III)400(Vn)
          4I0,32
          024,32+
          025,33
          400(H)                  β
          500(-4)
          504(Co)
          505(Co)
          4I0(AR)                 store matrix element = -4c_r c_t β
      JUMPI27

      I22)4I0,36                  matrix elements of type 2          β-type elements
          200,37                                                     between a locally
          270,35                                                     excited config-
      280(I26)                    acceptors not same                 uration and a
          200,35+                                                    transfer to it
          260,37+
          350,I2
      280(I26)                    vacated have opposite symmetry
          200(Q)
      290(II2)
          004,34+
          005,36+
      590(III)
      II2)004,36+                 prepare addresses for coefficients
          005,34+
      590(III)
      I25)4I0,36                  matrix elements of type 5          γ-type elements
          AR=0                              (γ-1)                    between two
      JUMP80,I≠J                                                     transfers in
          AR=-0.25EK              if diagonal element add            the same
                                        constant part                direction
      80)Hnv-4                    multiplier
          I06,I
          200,34
          370,2
      280(8I)
          002,35                  orbital coefficient addresses:
          003,37                   L  in B2
          004,34+                  L* in B3
          005,36+                  R  in B4
      590(82)                      R* in B5
      8I)002,34+
          003,36+
          004,35
          005,37
      82)200,37+
          260,35+
      590(68)
```

A117

```
123) 707,0
     417,32
     400,34
     707,0
     417,32
     002,32+
     003,33
     004,38+
     005,39
     AR=0
     Hnv8
     106,0
     200(P)
68)  400(Un)
     410,50
     210(Q)
     0=-1
     010(K)
58)  Y=0
     010(L)
     590(56)

57)  176,0
     080(88)
     200,*36+
     260,38+
     290(88)
     520,31.60
88)  514(Co)
     505(Co)
     420(Y)
     410(Y)
     124,1
     125,1
     L=L+1
     JUMP44,L≠T
     034(T)
     035(T)
     502(Co)
     503(Co)
     001(R)
     421(Ao)
     411(Ao)
     K=K+1
     122,1
     123,1
     JUMP58,K≠S

     401(Ao)
     520(Hn)
     411(Ao)
     JUMP127

120) JUMP41,I≠J
     AR=EK
     JUMP127

41)  410,32
     400(Un)
     410,50
     001,32+
     002,33
     003,34+
     004,33
     005,34+
     006,35
     200,33+
     260,35+
     327,0
     327,0
     260(P)
     210(P)
```

matrix elements of type 3 (γ2)

γ-type elements between a local L and a local R

orbital coefficient addresses as above

accumulator for $\sum_r$ multiplier

dimensions of γ-matrix (only row-length used)

accumulator for $\sum_t$

to compute one term

x $(-1)^{A_r \neq A_t}$ if type 3

accumulate $\sum_t$

repeat for t

accumulate $\sum_r$

repeat for r

matrix elements of type 0

γ-type elements between two locals of the same fragment

if diagonal use constant

coefficient addresses

a
b for $\sum_r$
c
b
c for $\sum_t$
d

add 4 x Q to P

A118

```
Y=0                          accumulator for Σ_r
200,34
280(42)
0=S
210,50
330,16                       both LL*
210,50+
010(K)
L=-16
590(70)
42)0=T
210,50+
320,16                       both RR*
210,50
K=16
010(L)
70)X=0
590(43)                      accumulator for Σ_t
                             to calculate term
72)200(Q)
290(53)
001,36+
061,38+                      x (-1)^(A_r ≠ A_t)
090(52)
520,31.60
52)512(Co)                   c'_br
505(Co)                      c'_ct
200(P)
340,0
340,0
210(Q)
410,32
590(71)

53)503(Co)                   c'_cr
504(Co)                      c'_bt
420,32
420,32
410,32
506(Co)                      c'_dt
420(X)                       accumulate Σ_t
410(X)
124,1
125,1
126,1                        t = t + 1
L=L+1
270,50+
280(44)

034(0)
035(0)
036(0)                       restart t
L=L-0
001,51
501(Co)                      recover a
420(Y)                       c'_ar
410(Y)                       accumulate Σ_r
121,1
122,1
123,1                        r = r + 1
K=K+1
270,50
280(43)
400(Y)
520(4)
410(AR)
200(P)
350,3
210(P)                       remove Q from P
JUMP127

43)011,51                    preserve a
56)001(K)
401(Uo)
410,38
```

```
                44)001(L)
A119            401(Vo)
                410,36
                001,39+
                021,37+
                011,32
                001,39+
                031,37+
            090(46)
            161,-1
            121,1
           46)011,32+
                200,39
                220,37
                210,33
                200,39
                230,37
            290(45)
            360,-1
            320,1
           45)210,33+
                340,0
                101,0
          47)071,32
            090(49)
            071,32+
          080(48)
            210,34
           48)220,51+
            121,1
          590(47)
          49)210,34+
            200,33
            340,0
            101,0
        85)071,32
          090(77)
          071,32+
        080(76)
          210,35
         76)220,51+
          121,1
        590(85)
        77)210,35+
          300,-1
          270(0)
        290(71)
          Q=P+512

         71)001,35
          007,35+
          401(Bo)
          001(Q)
          151,1
        080(50)
          427(Bo)
        590(51)
       50)437(Bo)
       51)001(Q)
          151,2
        080(55)
          520,31.60
       55)001,34
          431(Bo)
          007,34+
          001(Q)
          151,1
        080(87)
          437(Bo)
        590(78)
       87)427(Bo)
       78)200(0)
      290(72)
      590(57)

PSA
CLOSE
```

subroutine to produce a suitable combination of γ's from pair of atom position numbers r and t and details of the symmetry of the orbitals

generate in register 32 a set of distances:

32 $(y_r + y_t)$

32+ $|y_r - y_t|$

33 $(z_r + z_t)$

33+ $|z_r - z_t|$

generate adiresses relative to Bo of the four types of γ from the above set of y and z differences

34 γ^{LL}

34+ γ^{LT}

35 γ^{LJ}

35+ γ^{LJ}

$\gamma^{LL} + (-1)^z \gamma^{LJ}$

$= (-1)^g + 1$

$-(\gamma^{LL} + (-1)^z \gamma^{LJ})$