

"Instead of the cross, the Albatross

About my neck was hung"

[From the Rhyme of the Ancient Mariner
(Part II)]

S.T. COLERIDGE

(1772-1834)

EMPIRICAL APPRAISAL AND
GRAPH-THEORETICAL ASPECTS OF
SIMPLE THEORIES OF THE
"RING-CURRENT" EFFECT IN
CONJUGATED SYSTEMS

by

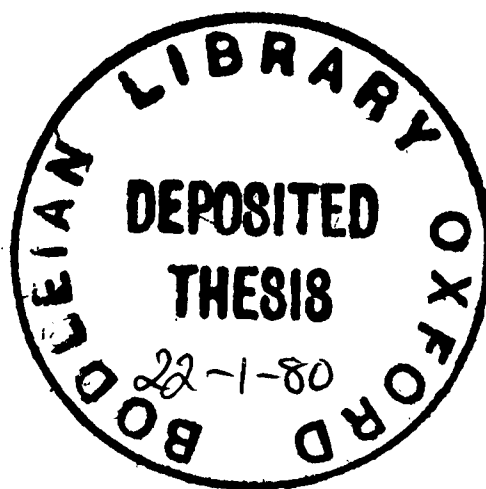
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A Thesis submitted for the Degree of
DOCTOR OF PHILOSOPHY
in the University of Oxford.

Department of
Theoretical Chemistry

Trinity Term, 1979

Christ Church



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DECLARATION

I hereby declare that no part of this Thesis has already been accepted, or is being concurrently submitted, for any degree in this, or any other, University.

Except where otherwise stated, and appropriate reference is made to the work of others, the material presented in this Thesis is the result of my own independent investigations carried out in the University of Oxford, and at Christ Church, Oxford.

(Signed)

----- Roger B. Mallion -----

R.B. MALLION

Dated -- April 26th, 1979

PREFACE AND ACKNOWLEDGMENTS

The idea of preparing and presenting this Thesis arose from discussions with the late Professor C.A. COULSON, F.R.S., in Michaelmas Term, 1972. This was the beginning of the second year of my five-year appointment as a Research Lecturer of Christ Church and we noted that, when a two-year Science-Research-Council Research-Fellowship (which had just determined) was taken into account, the total time for which I would have been in Oxford by the end of the Christ-Church Lecturership was comparable with the period spent in my original University (Wales). In order, therefore, to maintain a link with Oxford similar to that which I already had with the University of Wales, Professor COULSON agreed that I should do what he had done under similar circumstances when lecturing at the University of St. Andrews — that is, to submit some current research for a degree of the University. Accordingly, this Thesis was conceived, and Professor COULSON very kindly agreed to act formally as the Supervisor. In actual fact, the work was largely done independently, but I must record here how grateful I am for very useful collaboration and discussion with the late Professor COULSON concerning Chapter VIII and some of the material in Chapter VII. Furthermore, by no means all of the work I did during the above period is reported in this Thesis; much of my research activities at Oxford concerned abstract Graph-Theory, and only those parts of it that have a direct bearing on "ring-current" calculations (Chapters V-VII and Appendices C and D) are included here.

I should like to take this opportunity to express my deep gratitude to the late Charles COULSON, who brought to Theoretical Chemistry a quality of vision, warmth and kindness that only those who knew him could appreciate; to have been a Member of his Group at the Mathematical Institute, and then to have moved with him to his

Theoretical-Chemistry Department, represents the rarest of privileges. I have also been most touched by the encouragement and support that Mrs. Eileen COULSON has so willingly given, since her bereavement, to this project and others.

After Professor COULSON'S death (which occurred on January 7th, 1974), Dr. M.S. CHILD was kind enough to take over the formal position of Supervisor. Since we have not had technical discussions about the subject matter of this Thesis, Dr. CHILD must take no responsibility for its contents; I am, however, very grateful to him for the moral support he has freely given over a number of years.

I have now worked in the field which is the concern of this Thesis for over a decade and, during that time, I have had the privilege of meeting, and have benefited from correspondence and discussions with, most of the leading figures in it. That is why Chapter I is considerably longer than is customary in thesis introductions for, in addition to being (it is hoped) a comprehensive catalogue of previous papers in the field which will serve as an introduction to the new work to be described in the Thesis-proper, it is primarily intended to be a record of my own critique of those areas of the subject on which I have felt able to express a considered opinion, based on these several years in the field and on this contact with other workers, just referred to. The following, therefore, is an alphabetical list of some of those who, over the years, and to greater or lesser extents, have contributed, by discussion and/or correspondence, to the formulation of the ideas and opinions stated in Chapter I:

Dr. R.J. ABRAHAM,
Dr. A.T. AMOS, Mr. R.V.J. BUTT, Dr. D.W. DAVIES, Professor S.T. EPSTEIN,
Dr. J.A.N.F. GOMES, Mr. C.W. HAIGH, Professor G.G. HALL, Dr. M.L. HEFFERNAN,
Dr. J. HOARAU, Dr. P. LAZZERETTI, Professor R. McWEENY, the late
J.I. MUSER, Dr. H.G.F. ROBERTS, and Dr. A.J. SADLEJ.

The following list (likewise alphabetical) enumerates those with whom, over a similar period, I have had fruitful contact concerning mathematical Graph-Theory, which is the underlying theme of Chapters V-VII and Appendices C and D: Dr. A.C. DAY, Mr. C.W. HAIGH, Professor F. HARARY, Professor M. RANDIĆ, Mr. M.J. RIGBY, Dr. D.H. ROUVRAY, Professor G.S. RUSHBROOKE, Dr. A.J. SCHWENK, Professor N. TRINAJSTIĆ, the late D.A. WALLER, and Dr. R.J. WILSON.

Other academic acknowledgments are as follows:

for particularly exciting and instructive discussions on gauge factors (Chapter III and Appendix A) I thank Professor S.T. EPSTEIN; for correspondence on reactivity indices (Chapter IV) I am grateful to Dr. K.D. BARTLE and Dr. D.W. JONES; Mr. C.W. HAIGH was very stimulating in connection with the material presented in Chapter VII and Professor E. CLAR kindly provided experimental data which were invaluable for comparisons with theoretical predictions made in that Chapter; and, for helping to crystalise my ideas on strongly paramagnetic systems, I am indebted to Dr. G. EGE, Dr. J. GAYOSO, Dr. J.A.N.F. GOMES, Dr. M.C. GROSSEL, Dr. P. LAZZERETTI, Professor B.M. TROST, and Dr. H.W. VOS. The information or ideas arising from these exchanges are acknowledged in detail at appropriate points in the text.

If one person is to be thanked above all others I must single out for special mention Mr. C.W. HAIGH who, though we have not been in close contact in recent years, has always maintained an affectionate interest in my work, and has never failed to provide encouragement. It is with great pleasure that I dedicate this Thesis to him, and to his former teacher and mentor, the late Professor COULSON.

I should like to thank my College, Christ Church, for formally allowing me to keep Statutory Terms of Residence for this degree during the period of my Research Lecturership of the House — for the

tenure of which I am also most grateful, to the Dean, Canons and Students. I am further indebted to my colleagues and pupils at Christ Church for providing such a convivial atmosphere which, though nothing whatever to do with Graph Theory or "ring currents", was, nevertheless — by its very contrast — extremely conducive to their study!

Finally, it should be recorded that this Thesis could not have been produced without the valiant help of Mrs. Fiona FINLAYSON, who typed half of it, and Mrs. Margaret PALMER, who finished the job when Mrs. FINLAYSON returned to Australia. Because of my absence from Oxford, and my current occupation outside the academic sphere, the Thesis has been in production for a considerable period, but these ladies have been most patient with, and tolerant of, a somewhat finicky author who has by no means always been prompt in providing his copy. I am very grateful to both of them.

R. B. MALLION

No. 7, The Precincts,
CANTERBURY.
April, 1979.

A Statement on Units

With the exception of a small number of papers published within the last few years, the extensive Literature on the semi-empirical calculation of the magnetic properties of conjugated molecules — and particularly on the "ring-current" concept — has been presented entirely in terms of the (unrationalised) CGS-system of magnetic units.

In the main body of this Thesis, however, (from Chapter II onwards), when discussing actual numerical-quantities for a particular molecule, we shall almost invariably be dealing with ratios of these quantities, with respect to the corresponding values of them calculated for benzene; this applies to "ring-current" intensities in the i^{th} ring of an arbitrary, polycyclic molecule (J_i/J_{benzene}), "ring-current" contributions to overall molecular magnetic-susceptibilities ($\chi_{\perp}^{\pi \text{ London}}(\text{molecule})/\chi_{\perp}^{\pi \text{ London}}(\text{benzene})$), and "ring-current" secondary-fields at a given point r , (B'_r/B'_{benzene}), where B'_{benzene} is the secondary magnetic-field at a standard benzene-proton, due to the (unit) "ring-current" in benzene. To this extent, therefore, the essential discussion in this Thesis is independent of the particular system of units the reader cares to think in.

However, in Europe at least, it is now becoming more customary to use the so-called Système International d'Unités (perhaps something of a misnomer since it has not been widely adopted in, for example, the United States, a major contributor to the field dealt with in this Thesis.) This has, therefore, given rise to the dilemma of whether to present the formal theory of "ring currents" in Chapter I (and extensions and discussions of it in Chapters II, III, VI, VII and elsewhere) in the traditional CGS-system, or in 'SI'-units. After some deliberation, I have decided to take advantage of my intention to present (in Chapter I) a detailed, systematic and uniform historical-review of the

"ring-current" effect, to write the formal theory which arises in the course of this in units of the Système International — and then to continue with 'SI'-units throughout the Thesis. As a result of this policy, which has not been adopted without some misgivings, many of the well-known and standard equations of "ring-current" theory may have an unfamiliar air about them even to seasoned workers in this field. For their convenience, therefore, and for that of others more at home with the long-established system, I have also given the more-important equations of the theory as footnotes, in CGS-units. It is appropriate to make reference at this point to the preface on units in Atkins' book^{*}, and to the Royal Society's "Symbols, Signs and Abbreviations"[†], on which the former is based.

* P.W. Atkins, "Molecular Quantum-Mechanics", Parts I and II, pp xiv-xvi, Clarendon Press, Oxford, United Kingdom, 1970.

† "Symbols, Signs and Abbreviations", The Royal Society, London, United Kingdom, 1969.

EMPIRICAL APPRAISAL AND GRAPH-THEORETICAL
ASPECTS OF SIMPLE THEORIES OF THE
"RING-CURRENT" EFFECT IN
CONJUGATED SYSTEMS

By

R. B. MALLION

Christ Church, Oxford

D.Phil. Thesis

Trinity Term, 1979.

Abstract for the Association of Special Libraries and Information Bureaux*

This Thesis reports an empirical and mathematical appraisal of simple theories of the "ring-current" effect in conjugated systems; it is divided into five parts. Part One gives an extensive historical and critical review of the subject. In Part Two, the empirical utility of simple "ring-current" theories is assessed by confronting their predictions with experimental data on the alternant, condensed, benzenoid hydrocarbons. In Part Three, the mathematical techniques of graph theory are used to investigate the topological aspects of simple "ring-current" calculations and these considerations are exploited in order to rationalise the relative magnitudes of the "ring-current" intensities calculated, via the London-McWeeny method, in arbitrary, conjugated hydrocarbons. Part Four considers the success of "ring-current" approaches, of varying degrees of sophistication, when applied to strongly paramagnetic conjugated-systems. Part Five summarises the general conclusions and assesses the present status of "ring-current" calculations and their possible future-use. For calculations of the relative, intramolecular "ring-current" ^1H -NMR chemical-shifts in the specially parametrised case of the condensed, benzenoid hydrocarbons, even the crudest "ring-current" models may be used with considerable confidence, but calculations on strongly paramagnetic systems are likely to be realistic only if they are based on a wave function that is iteratively self-consistent with respect to resonance integrals and calculated bond-

orders. It is concluded that there is not much further headway to be made in the domain of π -electron semi-empirical calculations and that the future probably lies with ab-initio methods, or, at least, with all-valence-electron semi-empirical ones. In the final analysis, therefore, the "ring-current" idea seems destined to remain only a semi-quantitative conceptual-aid in the context in which, by very definition, it belongs — namely, that of semi-empirical, π -electron theory.

* This is the short abstract required for the Association of Special Libraries and Information Bureaux. The main (more-detailed) abstract is on page x.

ABSTRACT *

This Thesis reports an empirical and mathematical appraisal of simple theories of the "ring-current" effect in conjugated systems; it is divided into five parts. Part One (Chapter I) gives an extensive historical and critical review of the subject which, as well as serving as an introduction to the new work to be described in the Thesis-proper, is primarily intended to be a considered and uniform critique of all previous "ring-current" theories.

In Part Two, (Chapters II-IV) the empirical utility of simple theories of the "ring-current" effect is assessed by confronting their predictions with accurate and consistent experimental ^1H -NMR chemical-shift data on the alternant, condensed, benzenoid hydrocarbons. The classical Waugh-Fessenden-Johnson-Bovey approach is tested in Chapter II, although the required relative "ring-current" intensities in the various rings of the 16 different planar, condensed, benzenoid hydrocarbons studied are those calculated via the quantum-mechanical formalism due to London, Pople and McWeeny. A very satisfactory correlation is obtained (correlation coefficient: 0.96) between calculated and experimental ^1H -NMR chemical-shifts for 66 chemically non-equivalent but sterically unhindered protons in the 16 molecules dealt with. In Chapter III, the same experimental data are correlated with the predictions of another semi-classical formalism, in which the relative "ring-current" intensities are again calculated quantum-mechanically, by the London-Pople-McWeeny method, but the necessary geometric-factors are obtained on this occasion by means of a classical method based on the Biot-Savart Law. This 'Biot-Savart' formalism arises quite naturally when attempts are

* This is the main abstract. The shorter abstract required for the Association of Special Libraries and Information Bureaux is on page viii.

made to develop an empirical theory of proton chemical-shifts for arbitrary, conjugated molecules, without making appeal either to a 'test' dipole or to the current-density operator. The approach described has the further attractive feature that McWeeny's controversial insertion of a dipole contribution into the vector potential appearing in the gauge factor is avoided. McWeeny's procedure, whilst having no effect on the calculated "ring-current" intensities, is shown to be algebraically analogous (and, at large distances from ring centres, numerically equivalent) to estimating the secondary field at the origin due to a set of classical line-currents, as discussed originally by Longuet-Higgins and Salem. These 'line currents' are shown to be of the same magnitude as the quantum-mechanical 'bond-currents' implicit in the "ring currents" calculated by use of the simpler gauge-factors originally due to London, but their contributions to the secondary magnetic-fields experienced by the peripheral protons are here estimated classically by means of the Biot-Savart Law. Predictions of this formalism also compare well with experimental ^1H -NMR chemical-shifts (correlation coefficient: 0.98) — even though the estimate of the "ring-current" contribution to the downfield shift of a benzene proton (ca. 1.21 ppm) which this correlation gives rise to is very different from the value (of ca. 1.56 ppm) obtained when the same experimental data were regressed against predictions of the original McWeeny-theory (in which a dipole contribution was included in the gauge factor.) It is concluded that any further illegitimacy involved in the procedure of inserting a dipole contribution into the gauge factor is evidently quite simply compensated for, numerically, by an appropriate empirical-parametrisation. Such empirical parametrisations are also thought to absorb errors due to all the other various approximations of the "ring-current" theories (with apparently unwarranted efficiency) and they should, accordingly, be treated with more scepticism than has previously been

thought necessary. In the final chapter of Part Two, Chapter IV, the same experimental data are used to dispose of Kuthan's proposition that correlations exist between ^1H -NMR chemical-shifts in the condensed, benzenoid hydrocarbons and the several 'reactivity-indices' at the corresponding carbon-atoms to which the peripheral protons are bonded.

In Part Three (Chapters V-VII), the mathematical techniques of graph theory are used to investigate the topological aspects of simple "ring-current" calculations on conjugated systems. Once Chapter V has introduced the relevant terminology Chapter VI applies it to consider the graph-theoretical aspects of the simple London-Pople-McWeeny theory. There is a close connection between the adjacency matrix of the graph representing the σ -bond skeleton of the carbon atoms comprising a given conjugated-system, and the secular equations that arise in the theory (a relationship now well known to be common to all formalisms based on Hückel 'topological' molecular-orbitals) but in addition it is here emphasised that several other graph-theoretical ideas — notably those concerning circuits and spanning trees — specifically underlie the "ring-current" concept. In this connection, the question of whether or not a given molecular-graph is path-Hamiltonian is of prime importance, and it is pointed out that the unitary transformation proposed by McWeeny applies to path-Hamiltonian molecular-graphs, whereas one recently devised by Gayoso and Boucekkine can be applied to any simple, connected graph — as also can an explicit "ring-current" formula presented in Chapter III. It is concluded that although much graph theory is inherent in the "ring-current" concept, the "ring-current" index itself is not a completely topological quantity — even when a purely topological wave-function (such as the simple Hückel one) has been used to calculate it. Chapter VII then succeeds in providing a theoretical basis for relating the incidence of relatively 'high' and 'low' "ring-current" intensities (as observed, for example, in the central rings of peropyrene (XVII) and

perylene (XII), respectively) to intuitive Valence-Bond-Resonance-Theory (VB-RT) ideas about 'bond fixation'. It should be noted that this aim is not achieved by devising a "ring-current" formalism which is itself actually based on a VB-RT wave-function; the philosophy adopted here is (a) to identify, and classify, those situations in which simple MO-theory predicts specific rings in conjugated hydrocarbons to have exceptionally high or low "ring-currents", and then (b) to use topological arguments which rely simply on the carbon-atom connectivities of the conjugated systems in question to show that the situations identified in (b), above, are just those in which the absence, or presence, of VB-RT 'bond-fixation' is to be expected.

Part Four (Chapter VIII) considers the success of several "ring-current" approaches, of varying degrees of sophistication, when applied to strongly paramagnetic conjugated-systems. The prototype molecule for these calculations is pyracylene, a non-alternant hydrocarbon with a $4n$ -periphery, considered by Trost et al. to be a "perturbed [12]-annulene". It is concluded that if the results of calculations on unambiguously diamagnetic conjugated-systems are expressed as a ratio to the corresponding quantities calculated (by the same method) for benzene, even the crudest "ring-current" models may be used with considerable confidence. Calculations on strongly paramagnetic systems, however, will afford the possibility of realistic results only if they are based on a wave function that is iteratively self-consistent with respect to resonance integrals and calculated bond-orders.

Part Five (Chapter IX) summarises the general conclusions and assesses the present status of "ring-current" calculations, and possible future-directions in their use. It is concluded that there is not much further headway to be made in the domain of π -electron semi-empirical calculations and that the future probably lies with ab-initio methods -

or, at least, with all-valence-electron semi-empirical ones. In the final analysis, therefore, the "ring-current" idea seems destined to remain only a semi-quantitative conceptual-aid. This is not, in any way, to deprecate the "ring-current" notion, nor to deny its aesthetic and practical utility, but is merely to place it in the context in which, by very definition, it belongs — namely, that of semi-empirical, π -electron theory.

PART ONE

INTRODUCTION:

HISTORICAL AND CRITICAL
REVIEW OF THE "RING-CURRENT"
EFFECT

CHAPTER I

HISTORICAL AND CRITICAL REVIEW OF THE "RING CURRENT" EFFECT*

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* This Chapter is currently in press, almost verbatim, as a review of the "ring-current" effect in Progress in Nuclear-Magnetic-Resonance Spectroscopy.

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CHAPTER I

HISTORICAL AND CRITICAL REVIEW OF THE "RING-CURRENT" EFFECT

1.1 Introduction

This Thesis deals primarily with one of the major factors determining the magnetic properties of conjugated molecules — the so-called "ring-current" effect. Although the "ring-current" concept has its origins in the mid-1930's, it is only within the last 15-20 years that the expression has gained common currency, not only in Organic Chemistry, but in Physical and Inorganic Chemistry, and in Biochemistry and Biology. When, in the 1920's and 1930's, several groups of crystallographers were measuring the magnetic-susceptibility tensors of aromatic-hydrocarbon crystals, such experiments were far removed from the concerns of most chemists of the period. Even when several theories were devised¹⁻³ to explain these phenomena quantitatively — one of them³ involving the new Wave Mechanics — little interest seems to have been aroused outside a very limited circle. However, at the end of the post-war decade which saw the first successful demonstration of nuclear magnetic-resonance in bulk matter, it was realised that the unusual chemical-shifts of benzenoid protons were closely related to these earlier ideas. Not long afterwards, organic chemists were freely using "ring-current" terminology, and by now the concept is familiar to first-year undergraduates.

In this Thesis, we shall concentrate almost exclusively on simple theories of the "ring-current" effect, assessing (in Part Two) their empirical utility in contemporary Chemistry by placing particular emphasis on confrontation of their predictions with experimental data derived principally from proton nuclear-magnetic-resonance-(¹H NMR) spectroscopy. Some discussion of "ring-current" contributions to the magnetic susceptibilities of conjugated systems will inevitably be included

since, as was noted briefly above, such phenomena were historically the first to be interpreted in terms of a "ring-current" model; no specific study will be made here of "ring-current" contributions to the Faraday effect in polycyclic, conjugated molecules; (for a recent qualitative review of this, see ref. 4). More abstractly, (in Part Three of the Thesis) extensive consideration will be given to certain pure-mathematical (graph-theoretical) aspects of simple "ring-current" calculations on conjugated systems. The final section of the Thesis (Part Four) will be devoted to those molecules for which the simple semi-empirical theories of the "ring-current" effect begin to become inadequate — non-alternant hydrocarbons and strongly-paramagnetic conjugated systems.

Before discussing, in the succeeding sections of this Chapter (§§1.3 and 1.4), the historical development of "ring-current" theories (with particular emphasis on the simplest and most widely used of them), a brief review will be given in §1.2 of some qualitative uses and ramifications of the "ring-current" concept in ^1H NMR spectroscopy.

1.2 Qualitative Aspects of "Ring-Current" Effects in ^1H NMR-Spectroscopy

In this section we shall attempt briefly to outline the wide range of chemical studies to which the "ring-current" concept has had some qualitative relevance. Although the first application of these ideas to proton magnetic-resonance was made only in 1956, it is interesting to note that by 1959 a start had been made on nearly all the principal topics which will be listed here.

In 1953, Meyer et al.⁵ observed that the proton chemical-shift in benzene was some $1\frac{1}{2}$ ppm downfield of that for ethylenic protons. In 1956, Pople⁶ explained this using Pauling's¹ simple, classical model of a circulating π -electron current which gives rise to a small magnetic-field opposing the external one, and makes the benzene proton less

shielded — i.e. makes it resonate at lower field (or higher frequency).

This crucial paper led to a rapid increase in applications of this simple idea to similarly conjugated molecules. In the same year, Pople, with Bernstein and Schneider⁷, obtained the first ^1H -NMR spectra of several condensed, benzenoid hydrocarbons, and showed that the "ring-current" model could explain the very low-field resonances which were sometimes obtained. In substituted monocyclic and polycyclic benzenoid-hydrocarbons, it was found that many and varied substituent-effects had to be superposed on this "ring-current" effect in order to account for the observed chemical-shifts⁸. Bernstein et al.⁹ also examined azulene, a non-alternant hydrocarbon; here, the uneven charge-distribution (resulting from the inapplicability of the Coulson-Rushbrooke theorem¹⁰) added a significant perturbation to the "ring-current" effect. Similarly, in heterocyclic, unsaturated compounds such as pyridine¹¹⁻¹² and quinoline¹³, the low-field absorption was again taken to be indicative of a "ring current", but consideration now also had to be given to the electronegativity of the ring nitrogen-atoms and to the effect of their lone pairs.

The simple "ring-current" model predicts that if it is possible to have a nuclear spin inside a ring, it will suffer an opposite, high-field shift. The macrocycle of the porphyrins is large enough to allow such internal protons, and indeed the protons bonded to the pyrrole nitrogens were duly found to resonate at unprecedentedly high fields¹⁴. A further prediction of the simple model is that a nucleus held above a benzenoid ring will also suffer a high-field shift. As early as 1957, Waugh and Fessenden¹⁵ found that those methylene protons in para - 1,4 - polymethylene benzenes which were forced to lie close to the benzene ring and above it experienced a strong upfield-shift. This phenomenon has been of great assistance in the rapidly developed field of the cyclophanes¹⁶.

"Ring-current" effects on proton shifts have played a crucial part

in elucidating the chemistry of the annulenes. Initially, the only neutral annulene known was benzene, as the severely non-planar cyclo-octatetraene may be excluded from consideration. The 6π -electron monocyclic-ions $C_5H_5^-$ and $C_7H_7^+$ were, however, known and their ^1H -NMR spectra were recorded in 1957¹⁷. (As with non-alternant, neutral hydrocarbons, it was necessary to take account of the π -electron charges as well as the "ring-current" intensities, in order to rationalise the observed shifts of these species.) More annulenes soon became available and at first their proton shifts¹⁸ showed a pattern only roughly in agreement with simple "ring-current" theory; gross discrepancies disappeared, however, when the conformational mobility of some of these compounds was realised, and low-temperature spectra were obtained where necessary. The higher analogues of benzene, the $[4n + 2]$ - annulenes and their polydehydro-derivatives, showed very low-field absorption for outer protons, and very high-field absorptions for inner protons, as for the porphyrins. An interesting new phenomenon also appeared, (the theoretical explanation of which followed later¹⁹⁻²⁵), namely that the $[4n]$ - annulenes showed a diametrically-opposite effect, the outer protons absorbing to high field, the inner protons to low field. Compounds exhibiting the commoner, diamagnetic "ring-current" have now been dubbed 'diatropic', while those with the reversed, paramagnetic current are called 'paratropic'^{26,27}. Recent reviews are available^{25,27,28}. Compounds which may be regarded as condensed, polycyclic annulenes, or 'perturbed'²⁹ annulenes, also reflect this "ring-current" behaviour. The first recognised³⁰ as having a paratropic ring was biphenylene, which might be regarded as dibenzo- $[a,c]$ - $[4]$ - annulene. The question of paramagnetic "ring-currents" in 'perturbed' $[12]$ - annulenes has been one giving rise to considerable speculation in recent years^{29,31-34} and is the particular concern of Chapter VIII of this Thesis.

If benzene rings are successively condensed onto phenanthrene,

but always in angular rather than linear fashion, the steric interactions present when these further rings are added cause distortion to a non-planar geometry and subsequent members of the series are severely non-planar. These remarkable³⁵⁻³⁸ compounds are appropriately termed 'helicenes'; if phenanthrene is regarded as [3] - helicene, the largest such compound so far synthesised is [13] - helicene³⁷. The peripheral protons in these (fully conjugated but non-planar) compounds suffer downfield "ring-current" shifts from their own and adjacent rings, and also upfield shifts from the rings above which they are situated, so that their ^1H -NMR is of particular interest³⁵⁻⁴⁰.

The widest use of "ring-current" ideas has been in deducing configurational and conformational information about complex structures⁴¹, particularly in the field of Biological Chemistry, when nucleotides, many vitamins, enzyme-prosthetic groups and co-enzymes are encountered which contain various conjugated-heterocycles (e.g. ref. 42). In polypeptides and small proteins, the "ring-current" effects of tryptophan, histidine, phenylalanine and tyrosine can, in favourable cases, be used to make deductions about tertiary structure⁴³⁻⁴⁶.

Only intramolecular effects have so far been considered; "ring currents" can, however, also exert intermolecular effects. Practicing NMR-spectroscopists have long known and capitalised upon the striking effects on proton shifts of using aromatic solvents such as benzene, or of adding more-limited quantities of benzene to a solution. These depend not only on the "ring-current" effect per se, but on differential mean-proximity and mean-orientation (which may or may not involve complexation) both as between protons within the substrate molecules, and also between substrate protons and protons of the internal reference-standard. When the diatropic benzene is used, the shifts (compared with the 'inert' reference) are always to high field⁴⁷. Such shifts have been called 'ASIS' ('Aromatic Solvent-Induced Shifts')^{48, 49} and they

have even been used to devise a scale (the S-scale) of "ring-current" effects⁵⁰. If such intermolecular effects are sufficiently large (as with porphyrins, for example) these species have been further dubbed 'diamagnetic shift-reagents'⁵¹ by analogy with the now very-well-known, paramagnetic lanthanides. In the field of Biochemistry, one can monitor not only the intramolecular "ring-current" effects of the 'stacking' of the conjugated bases in a dinucleotide (see, for example, ref. 52), but also the intermolecular effects of the intercalation of purines into dinucleotides⁵³⁻⁵⁵.

If a conjugated system has any tendency to self-association then its own intermolecular "ring-current" effect will give differential chemical-shift variation when the solution is diluted, and some interesting examples (including biochemical ones) have been reported^{46,56-62}. Intra-molecular "ring-current" effects have also been used to investigate dilution shifts in conjugated systems⁶³. Intermolecular "ring-current" effects arising from chiral α -naphthyl species have even been used for the determination of optical purity and absolute configuration^{64,65}.

In the discussion so far, the author has been careful to use terms such as "conjugated molecule" rather than "aromatic molecule", for it is not the intention of this Thesis to enter into the wide-ranging (and one might even say 'semantic') controversy which has arisen concerning an alleged connection between "ring currents" and "aromaticity". As early as 1961, it was the striking "ring-current" effects on proton chemical-shifts which led to the suggestion⁶⁶ that these become a new criterion of "aromaticity", rather than those then extant. Furthermore, those species which, as a result of their ^1H -NMR spectra, have been called paratropic^{26,27} have been described⁶⁷ as "anti-aromatic" in a wider sense. Since then there has been a further proliferation of 'hyphenated' aromaticities⁶⁸; reference is merely made here to recent symposia⁶⁸⁻⁷⁰, books^{26,71}, and reviews^{4,41}. The late S. Winstein^{69c} has interpreted the diamagnetic exaltation⁷² and ^1H -NMR of the 'homo-aromatic'⁷³ homotropylium ion in

terms of a 6π -electron "ring-current". The same school⁷⁴, and others⁷⁵⁻⁷⁸, have even written of a "ring current" in cyclopropanes, which can only be called "aromatic" (with or without hyphenation!) by yet a further stretching of the meaning of this term⁷⁹. Although it has been quite vehemently criticised⁸⁰⁻⁸², the proposed correlation between "aromaticity" and "ring currents" is, even now, much invoked, the latest instance being in a recent study⁸³ of the "aromatic character" of certain five-membered heterocyclic systems.* The present view is nicely summarised by Benassi et al.⁸⁴ who, in a recent paper, have addressed themselves to the whole question of magnetic criteria for "aromaticity". The present writer's opinion on the connection between "ring currents" and "aromaticity" has been more explicitly detailed elsewhere²⁸.

This discussion has so far been exclusively in terms of ^1H -NMR, and the magnetic-resonance applications of "ring-current" theories treated in this Thesis will be confined entirely within that realm. Since "ring-current" effects, expressed in ppm, are expected to be independent of the isotopic species being shielded, and as the magnitude of effects other than those due to "ring currents" is so much greater for all other nuclei, isolation and identification of "ring-current" contributions is likely to be very much more difficult in non-proton NMR^{28,85}. Some suggestions of "ring-current" effects in ^{13}C -NMR spectra have, however, been made^{86,87} and it must be admitted that the low-field shift recorded⁸⁷ for the central carbons in the (paratropic³⁰) four-membered ring of biphenylene, for example, is indeed striking. However, Abraham et al.⁸⁸ have recently warned of the dangers of using ^{13}C chemical-shifts, without further supporting evidence, to determine such a 'subtle'⁸⁸ problem as 'aromatic delocalisation', while Günther et al.⁸⁹ have pointed out that attempts to use ^{13}C data as criteria for "aromaticity" are 'not without risk'²⁸.

In this subsection, an attempt has been made to illustrate, however cursorily, to what a wide range of chemical phenomena "ring-current" ideas

* See also Appendix E.

have been applied at the qualitative level; in the succeeding sections of this Chapter, and in the remainder of this Thesis, we turn to more-detailed, quantitative aspects of the "ring-current" concept, and its applications.

1.3 Classical and Semi-Classical Theories of the "Ring-Current" Effect (i) Magnetic Susceptibility

For historical reasons, as has already been seen (§1.1), the story of "ring currents" starts with bulk- (rather than nuclear) magnetism. The (volume) magnetic-susceptibility tensor is defined by

$$\underline{\underline{M}} = \underline{\underline{\chi}}^v \underline{\underline{B}} \quad (1.1)$$

where $\underline{\underline{M}}$ is the magnetisation vector and $\underline{\underline{B}}$ is the magnetic-flux density (both of dimensions $[MT^{-1} Q^{-1}]$); $\underline{\underline{\chi}}^v$ is thus dimensionless. The commonly-used molar magnetic-susceptibility-tensor is related to it by

$$\underline{\underline{\chi}}^m = (M/d) \underline{\underline{\chi}}^v \quad (1.1a)$$

(where M is the molecular weight and d is the density). Its dimensions are, accordingly, $[L^3] \text{ mole}^{-1}$. Essentially the whole of the voluminous literature uses the unrationalised CGS-system, in which the units become $\text{cm}^3 \text{ mole}^{-1}$; the commonly-used abbreviations are CGS-emu or just CGS-units. All values turn out to be somewhat more than 10^{-6} of these units.

To convert to

the (rationalised) units of the Système International (SI), the factor is

$$\underline{\underline{\chi}}^{m,\text{CGS}} / (\text{cm}^3 \text{ mole}^{-1}) = (1/4\pi) \times 10^6 \times \underline{\underline{\chi}}^{m,\text{SI}} / (\text{m}^3 \text{ mole}^{-1}).$$

In quantum-mechanical calculations, we shall be more-directly concerned with evaluating the molecular magnetic-susceptibility-tensor, $\chi_{\alpha\beta}$,

$$\chi_{\alpha\beta} = -\mu_0 \left(\frac{\partial^2 E}{\partial B_\alpha \partial B_\beta} \right) \quad \begin{matrix} B_\alpha \\ B_\beta \end{matrix} = 0 \quad (1.2)$$

where E is the molecular energy in the presence of the field B . $\chi_{\alpha\beta}^m$ and $\chi_{\alpha\beta}$ are merely related by Avogadro's number; when the distinction between these two quantities is not particularly material, the superscript 'm' will frequently be omitted.

These tensors can be diagonalised by an orthogonal transformation to principal axes, of which in many cases either one or all three are determined by symmetry. In this Thesis, we are concerned, for the most part, with planar molecules, and we shall always define the molecular z -axis as being perpendicular to the molecular plane; it will of course always be a principal axis. In general, two anisotropies can be defined; however, for planar molecules we shall use the term the anisotropy, which we define as

$$\Delta\chi^m \equiv \chi_{zz}^m - \frac{1}{2} (\chi_{xx}^m + \chi_{yy}^m) \quad (1.3)$$

(but see also refs. 90-94).

In an isotropic medium (liquid, solution, gas) what is measured is the mean, molar, magnetic susceptibility

$$\bar{\chi}^m = \frac{1}{3} (\chi_{xx}^m + \chi_{yy}^m + \chi_{zz}^m) = \frac{1}{3} \text{tr } \underline{\chi}^m \quad (1.4)$$

(and when no ambiguity will result the bar superscript will be omitted).

Far more mean-values have been measured than full tensors or anisotropies; and very early in the development of this field it was found that, to a remarkable degree, they were additive, being sums of atomic terms plus some 'constitutive' corrections^{95,96} (see also Chapter 6 of ref. 90). Any deviations from these (Pascal's) rules is said to be a measure of 'magnetic exaltation'.

(ii) The Earliest Period

Although the susceptibility tensors of diamagnetic species were being examined at least as early as 1883⁹⁷, it was not until the 1920's that the magnetic properties of conjugated ("aromatic") hydrocarbons were systematically investigated. Raman and Krishnan⁹⁸ considered the magnetic double-refraction (Cotton-Mouton) effects exhibited by liquid benzene, on the basis of the Langevin theory of diamagnetism⁹¹. These experiments, and many later ones⁹⁹⁻¹⁰², showed that cyclic or polycyclic conjugated-systems had magnetic susceptibilities of a distinctly different character from those of saturated (even though still, perhaps, cyclic) molecules such as

cyclohexane¹⁰². These molecules were found to exhibit an unprecedented magnetic-exaltation and also an unusually pronounced anisotropy^{98,2}.

Raman and Krishnan⁹⁸ concluded that the value of the Cotton-Mouton constant they measured for benzene could be explained only on the assumption that the susceptibility in the direction of the z-axis is about twice as large as in directions perpendicular to this axis; furthermore, they also drew attention to an analogous observation of Owen¹⁰³, and Honda and Sone¹⁰⁴, on the different magnetic-properties of carbon in diamond and in graphite. Diamond shows no magnetic anisotropy; graphite, on the other hand, shows a very large one, its susceptibility parallel with the hexagonal axis being about seven times as large as in perpendicular directions⁹⁸.

All this growing evidence concerning the "anomalous diamagnetism"¹⁰⁵ of conjugated systems prompted Raman to resurrect an earlier hypothesis of Ehrenfest¹⁰⁶ in an attempt to rationalise these experimental observations. Ehrenfest¹⁰⁶ had suggested that the high anisotropy of magnetic susceptibility of bismuth and antimony could be ascribed to the existence, in the metallic crystal-lattice, of "electron orbits of large area including several atoms within their radius" and this, in Raman's opinion¹⁰⁵, appeared to furnish "a very natural explanation of a variety of phenomena, which up to now have been obscure" — including the pronounced magnetic-anisotropy of graphite and of (poly)cyclic conjugated-hydrocarbons. A similar conclusion was also reached by Ubbelohde¹⁰⁷; commenting on the work of Iball and Robertson¹⁰⁸, which had shown that anthracene, chrysene and 1,2;5,6-dibenzanthracene had a "graphite structure with all the atoms lying in one plane", and bearing in mind the then-recent work of Hückel, Ubbelohde suggested that (what are now termed) the π -electrons in any one conjugated-ring "have a certain possibility of movement to other nuclei within the same molecule" and that this would lead (amongst other things) to an anisotropy in the magnetic susceptibility of such molecules.

Ubbelohde also suggested that the physical properties of large molecules with condensed "aromatic" nuclei would be of considerable importance in the theory of metallic bonding, 'delocalisation effects' in which were already being studied by Peierls¹⁰⁹.

(iii) The Concept of π -Electron "Ring-Currents"

At this period, the new wave-mechanical theories of Schrödinger and Heisenberg were being more widely appreciated. In spite of this, and the recent availability of Van Vleck's famous quantum-mechanical text on magnetism¹¹⁰, the first two quantitative papers on the magnetic properties of conjugated hydrocarbons, succeeding the qualitative ideas just discussed, were avowedly classical in approach. One was by Pauling¹ and the other, prepared independently, by the late Dame Kathleen Lonsdale².

Pauling observed¹ that (in, say, benzene) the π -electrons, by definition, occupy orbital wave-functions which are antisymmetric with respect to reflection in the molecular plane, and that the probability distribution-function for these electrons is large only in two "ring-shaped" regions above and below the molecular plane¹¹¹. Pauling postulated that, in these regions, the potential function representing electron interaction with the nuclei, and with other electrons in the molecule, would approximate to cylindrical symmetry with respect to the hexagonal axis of the molecule; with this arrangement, Pauling alleged that the electron, some distance above or below the plane of the nuclei, could pass "almost imperceptibly from the field of one carbon-atom to that of the next." That is, he assumed that, under the influence of the applied, external field, the π -electrons flow freely, producing inter-atomic 'currents'.

If, as was assumed, the π -electrons in the benzene ring are free to move as in a circular wire, the effect of an applied magnetic-field, B_0 , which we first consider to be perpendicular to the molecular plane, will be to induce uninhibited Larmor-precession corresponding to a current (for the

six π -electrons) of

$$I = - \frac{3 e^2 B_o}{2 \pi m} \quad (1.5)$$

(where e and m have their usual meanings). There results* a contribution to the molar magnetic-susceptibility tensor of

$$\chi_{zz}^m = - \frac{\mu_o 3N_A e^2}{2m} \cdot (\rho^2)_{av} \quad (1.6)$$

Here, N_A is Avogadro's number, and $(\rho^2)_{av}$ is the mean-square distance of an electron from the z axis, $\pi(\rho^2)_{av}$ thus being the area of the current loop. A current of this sort does not contribute to the other components of the susceptibility tensor, and equation (1.6) therefore also gives the "ring-current" contribution to the anisotropy, $\Delta\chi$. Using for $(\rho^2)_{av}$ the value a^2 , in which a is the distance from the axis to the carbon nuclei (1.39 Å), Pauling found the anisotropy contribution to be -49.2×10^{-6} CGS emu, in reasonably good agreement with the then-accepted experimental-value of -54 for the magnetic anisotropy of benzene (though a more-modern estimate¹¹² is -59.7).

In larger molecules these 'currents' were assumed to flow around the various rings of the polycyclic network of the hydrocarbon, and so eventually came to be termed "ring currents" (although it should be observed that, contrary to what has become common folk-lore in this field, Pauling himself never actually used this term!) In Pauling's approach¹, the analogy with classical "Kirchhoff" electrical-network calculations was

* These formulae are derived from the classical Langevin-scheme, which also has a basis in quantum mechanics (see, for example, ref. 91 on pp. 533-535).

carried further with the use of Kirchhoff's laws of currents at a junction in order to compute the actual sizes of these induced 'currents',^{1,111}.

(The relevance in "ring-current" calculations of some topological aspects of Kirchhoff's classical work on electrical networks will be examined in detail in Chapter VI).

Pauling's method has by no means been generally adopted, subsequently, to evaluate the individual "ring-current" intensities in polycyclic molecules. Abraham's 1961 calculation¹¹³ of the "ring-current" intensities in porphyrins seems to be the only example of trusting application of the method; it actually resulted, after some empiricism, in very good agreement with some experimental magnetic-properties. The Pauling model has also been used by Maddox and McWeeny¹¹⁴ — but only to show that it predicts unreasonably high magnetic-anisotropies and "ring-current" intensities in large polycyclic-molecules, when compared with the theoretical predictions of even the simplest³ quantum-mechanical approaches.

We now turn briefly to the (classical) "ring-current" calculations of Lonsdale², who, by 1936, had for some time been "engaged on a determination of ... diamagnetic constants ... with the object of applying the theory of molecular orbitals to the quantitative explanation of diamagnetic anisotropy". She also pointed out that the idea that certain electrons can move in the way in which we are discussing "is implicit in the theory of molecular orbitals, as applied by Hückel¹¹⁵ to aromatic and unsaturated molecules".

Like Pauling, Lonsdale independently argued that the excess diamagnetism in the direction normal to the plane of the molecule "is due solely to, and is the entire contribution of, the precession of the π -electron orbits". She therefore used a formula which—allowing for a slight difference in notation—is essentially identical to that of Pauling, (equation (1.6)). By use of this expression, and the previously determined anisotropies of several conjugated-molecules, the average effective-radius of the π -electron orbits in benzene was estimated to be 1.5–1.6 Å (to be compared with 1.39 Å, the

radius of the benzene nucleus itself). In the condensed ring-systems, which are more diamagnetic than would be expected from a strict additivity-rule, the 'average orbital-area' of the π -electrons was found to be greater than this, though not actually equal to the area of the whole condensed-nucleus. Lonsdale concluded: "It seems likely, therefore, that, for such compounds, a large proportion of the π -electrons (or each π -electron for a large proportion of the time) occupy orbitals equal in area to a single benzene-ring, only a few occupying larger orbits."

(iv) Nuclear Magnetic Resonance

We now leave classical theories of bulk magnetism and consider ^1H -NMR for, as was observed in §1.2, twenty years after Pauling's and Lonsdale's papers, that of Pople⁶ revived interest in the "ring-current" idea by relating it to proton chemical-shifts.

For one type of (uncoupled) proton, the NMR-spectrum of which is observed in an isotropic medium, the familiar resonance-condition is

$$\begin{aligned} h\nu_0 &= g_p \mu_n B^{\text{local}} \\ &= g_p \mu_n B_0 (1-\sigma) \end{aligned} \tag{1.7}$$

The g -value of the proton, g_p , is 5.585; the nuclear magneton, $\mu_n = e\hbar/(2M_p)$, where M_p is the mass of the proton; B_0 is the uniform, external, magnetic field; and σ is the dimensionless shielding-constant for that proton. It should be noted that the scalar σ observed in isotropic media is actually one third of the trace of a tensor; in theoretical treatments, therefore, the three diagonal elements of this tensor have to be calculated. The local field at the particular proton can be written, following a very common practice which is certainly justified in a classical approach, as a series of terms; for a peripheral proton in a conjugated molecule:

$$\underline{B}^{\text{local}} = \underline{B}_0 + \underline{B}^{\text{core}} + \underline{B}' \quad (1.8)$$

Here, $\underline{B}^{\text{core}}$ derives from the inner-shell and σ -electrons and can be thought to include a local contribution from the π -electrons (even though this cannot rigorously be defined, even classically); and $\underline{B}'$ is the contribution from the induced π -electron "ring-currents". (At this stage, solvent- and other environmental effects are, of course, being neglected). Until recently, experiments were almost always conducted at constant frequency, and this has determined the commonly used terminology, which we shall retain in this historical review. If $\underline{B}'$ is positive, as for a benzene proton, then at constant frequency (and thus constant $\underline{B}^{\text{local}}$) a lower value of $\underline{B}_0$ is required for resonance. This term therefore makes the benzene proton resonate at comparatively low field. (The opposite is true, for example, for the cyclophane protons above a benzene ring which thus absorb at high field).

If the resonance position of the "aromatic" proton in question is subtracted from that of a hypothetical olefinic-proton (similar, perhaps, to the olefinic proton in cyclohexa-1, 3-diene),¹⁵ one may hope to eliminate both $\underline{B}_0$ and $\underline{B}^{\text{core}}$ in equation (1.8), for the localised effects should be very similar in the two cases; in this way, a direct estimate of $\underline{B}'$ could be obtained, if this assumption turned out to be justified. Comparing, for example, with (1.7), we define the dimensionless quantity^{*} $\Delta\sigma = \underline{B}'/\underline{B}_0$. For a benzene proton, then, a negative $\Delta\sigma$ implies de-shielding. Furthermore, when comparing theory and experiment for a variety of protons in benzenoid molecules, we shall frequently use the so-called 'sigma ratio', defined as $\Delta\sigma/\Delta\sigma_{\text{benzene}}$.

* Following common practice, we are using Δ in two senses in this Thesis. In $\Delta\chi$ it signifies the anisotropy in a tensor; in $\Delta\sigma$ it refers to the difference between two values of a scalar. As we are nowhere treating the anisotropy of the identical shift-tensor, no confusion should arise.

(v) Classical Theories of the "Ring-Current" Effect in ^1H -NMR(a) Pople's Point - Dipole Method

The first (and entirely classical) method of predicting $\Delta\sigma$ -values in benzene was suggested by Pople⁶. In this approach, the effect of the induced "ring-current" in benzene is assumed to be equivalent to that of a point dipole at the ring centre, of magnitude

$$M = IA \quad (1.9)$$

where A is the area enclosed by the current loop, and I is the "ring current" calculated on Pauling's free-electron model (equation (1.5), which assumed $\vec{B}_0$ to be along the z -axis). With the six electrons in the superconducting "current" flowing about a circular loop of radius a (the length of a ring C-C bond), $A = \pi a^2$, and the dipole causes a secondary field at the proton, distant R from the ring centre, of magnitude

$$B'_{zz} = \frac{\mu_0}{4\pi} \frac{M}{R^3} \quad (1.10)$$

With $\vec{B}_0$ in the plane, no contribution to the other diagonal-elements of the shielding tensor results; in order to obtain the net contribution to the isotropic shielding we therefore divide by three, obtaining:

$$\Delta\sigma = \frac{B'}{B_0} = -\frac{\mu_0 e^2 a^2}{4\pi 2m} \times \frac{1}{R^3} \quad (1.11)$$

For a polycyclic molecule, as a first approximation, the current in each ring is taken to be equal to the benzene current (which, of course, would certainly not be the case if the Pauling model¹ were rigidly applied; this approximation is, however, not a bad one^{114,116} and is usually more realistic than formally applying the Pauling model in its entirety.) In

this case

$$\Delta\sigma = \frac{-e^2 a^2 \mu_0}{2m} \sum_i \frac{1}{R_i^3} \quad (1.12)$$

where R_i is the distance from the centre of the i^{th} ring to the proton concerned. As has been mentioned already (§1.2), this simple and extremely crude model was found to account qualitatively for the observed proton chemical-shifts within a restricted range of polycyclic, conjugated hydrocarbons⁷.

(b) The Waugh-Fessenden-Johnson-Bovey Approach

The simple 'point-dipole' approximation of Pople⁶ was soon improved by Waugh and Fessenden¹⁵, and by Johnson and Bovey^{117,118}. They used Pauling's model¹ to calculate the "ring current" in benzene, but instead of approximating its effect to that of a point dipole, they calculated the secondary field due to a complete, classical current-loop, of radius equal to the length of a carbon-carbon bond in benzene. They further made allowance for the fact that the currents do not 'flow' in the molecular plane, but in loops, distance p above and below the plane — i.e. they considered the actual distribution in space of the π -electron currents. The value of p was considered to be an empirical parameter and since previous work¹⁵ had suggested that the "ring-current" contribution to the downfield shift of a benzene proton is approximately 1.5 ppm, p was adjusted so as to give this prediction for benzene; the value of p so found (0.64Å) was then used in all subsequent calculations. In this way, they calibrated their theory with respect to benzene¹¹¹.

From classical electromagnetic-theory¹¹⁹, the shielding, $\Delta\sigma$ (ppm), provided by n electrons circulating in a loop of radius a , at a point with cylindrical coordinates (ρ, z') (both measured in units of a) with respect to the centre of the current loop, is

$$\Delta\sigma = \frac{\mu_0 n e^2}{4\pi 6\pi m a} \frac{1}{[(1+\rho')^2 + (z')^2]^{\frac{1}{2}}} \left[K(k') + \frac{1-(\rho')^2 - (z')^2}{(1-\rho')^2 + (z')^2} E(k') \right] \quad (1.13)$$

in which

$$k' = \left(\frac{4\rho'}{(1+\rho')^2 + (z')^2} \right)^{\frac{1}{2}} \quad (1.14)$$

and is the modulus of the Complete Elliptic Integrals K and E.

This theory has been tested by several authors¹²⁰⁻¹²²; in particular, Dailey¹²² has usefully summarised the comparison of experimental ¹H chemical-shifts of condensed, benzenoid hydrocarbons with classical, semi-classical and quantum-mechanical theories, as he saw them in 1964. It was concluded that classical and semi-classical theories between them seemed incapable of giving a satisfactory and simultaneously coherent account of both magnetic susceptibilities and chemical-shift data. In Chapter II of the present Thesis, the whole question of the Waugh-Fessenden-Johnson-Bovey theory is re-examined in detail using more-recently acquired ¹H-chemical-shift data. Further discussion of the equations relevant to this theory, and of Dailey's evaluation of it, is therefore deferred until that Chapter.

The major triumph of this approach over the last 15-or-so years has been its application to highly shielded protons in more-complex molecules, where molecular geometry constrains certain protons to be held above the planes of conjugated rings, within what, on the point-dipole model, would be described as the 'shielding cone' of such a ring.

The very widespread application of the Waugh-Fessenden approach to conformational, and other, problems in Organic and Inorganic Chemistry and in Biochemistry has been due in no small measure to the tabulated shielding-values made available¹¹⁸ by Johnson and Bovey¹¹⁷ for a three-dimensional network of points around a standard, hexagonal ring of benzene dimensions. So universal^{*} is the use of these tables that the Waugh-Fessenden approach has now generally become known as the 'Johnson-Bovey model'.

A more-approximate version of the same model has also been used by Mayo and Goldstein¹²³. Instead of using the exact expression for the potential due to a current loop of radius a , they used a series expansion. The problem clearly has cylindrical symmetry: provided that $r > a$, where r is the distance of the point in question from the centre of the loop, a convenient expansion of the potential—and also of the resulting field—is in inverse powers of r , the corresponding coefficients being Legendre polynomials¹²³. For the problem with which they were concerned, the relevant values of (r/a) were sufficiently large that they truncated this expansion after the first two non-zero terms: it is this truncation which chiefly distinguishes their approach from that of the earlier part of this subsection. They manipulated the formulae to introduce the classical susceptibility instead of the classical current, obtaining, finally, the expression

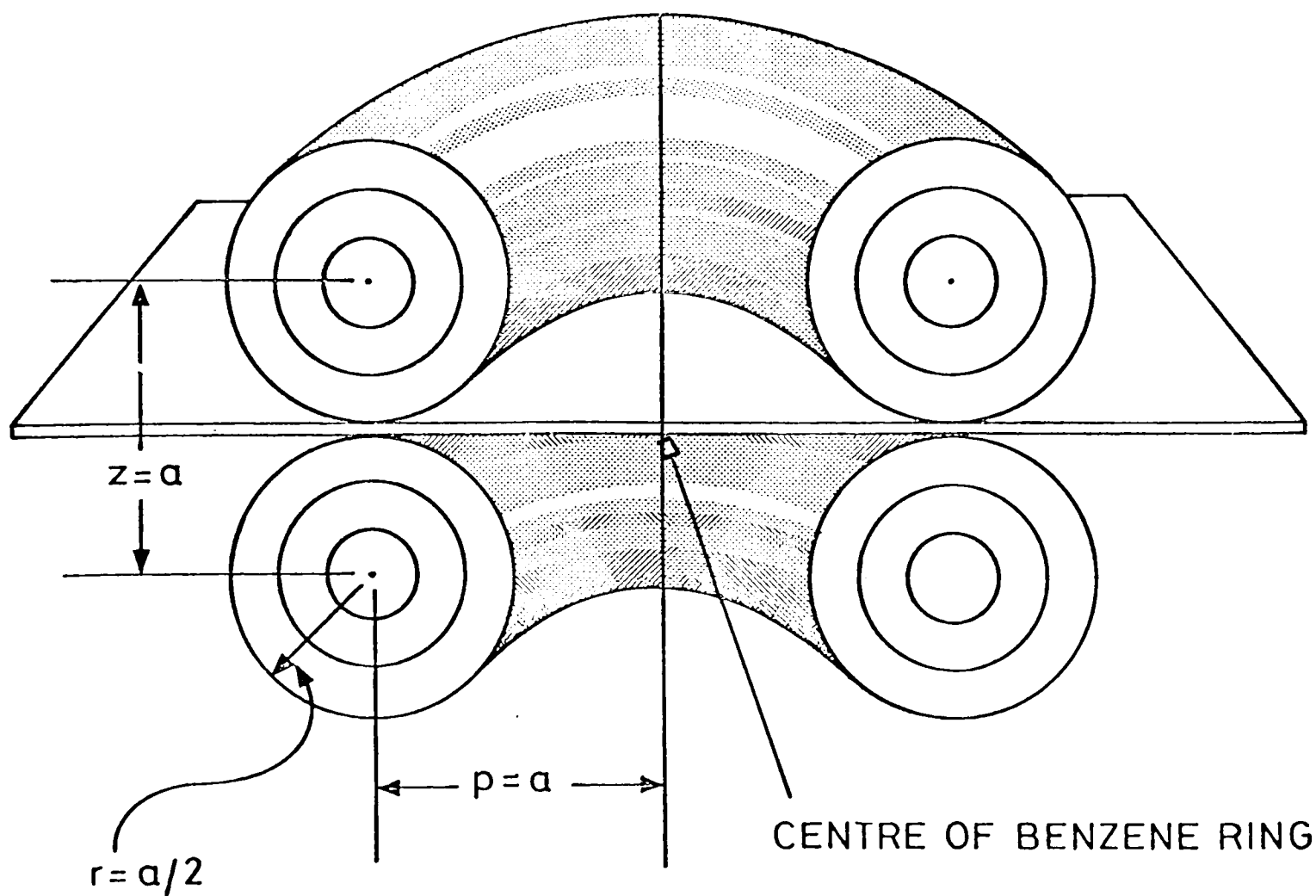
$$\Delta\sigma = \frac{\Delta\chi}{3r^3} \left[(1-3 \cos^2\theta) + \frac{3a^2}{8r^2} (35 \cos^4\theta - 30 \cos^6\theta + 3) \right] \quad (1.15)$$

Here, (r, θ, ϕ) are spherical polar co-ordinates with origin at the centre

*In support of this statement, it is of interest to note that in 1969, 10 years after its publication, ref 117 was cited 42 times, according to the Science Citation Index; in 1970 it was cited 63 times, in 1971, 55 times, in 1972, 53 times, in 1973 59 times, and in 1974, 60 times. The Johnson-Bovey paper is, therefore, cited in the literature, on average, about once per week.

FIGURE 1.1

Diagrammatic Representation of the Farnum-Wilcox Double-Torroidal-Shell
Model



of the loop, the axis being perpendicular to the loop. $\Delta\sigma$ is the chemical-shift contribution from one loop, and thus the effects of the two loops must be summed.

They calculated the multiplicative constant by assuming, in the case of a benzene proton, the rather large value $-\Delta\sigma = 1.95$ ppm, and separated the two loops by $1.4\text{\AA}$. Their particular application was to the case of biphenyl, with shieldings calculated as a function of dihedral angle. This method appears to have been little used, but ref. 124 provides a recent example of its application.

The most-recent systematic - application of the Waugh-Fessenden approach has been in an investigation which claimed to evaluate the relative importance of 'local-anisotropic' effects (§1.5) and "ring-current" effects on ^1H NMR shieldings in benzenoid hydrocarbons¹²⁵. Further (and critical) discussion will be devoted to this paper in §1.5 and in Appendix B.

(c) The Farnum-Wilcox 'Double-Toroidal-Shell' Model

In 1967, Farnum and Wilcox¹²⁶ put forward their "double-toroidal-shell" model. They pointed out that the most-complete classical-model for the "ring current" in benzene would involve the summation of an infinite set of current loops, each weighted (in a cylindrical-polar-coordinate system (ρ, z, ϕ)) according to the electron-density average for all pairs of ρ and z (*i.e.* by averaging over all ϕ for each such pair).

Farnum and Wilcox proposed several possible simplifications for the model, finally adopting a toroidal shell of circular cross-section (see Figure 1.1) with an outer radius $\rho = a/2$, and a cross-sectional radius $r = a/2$. They then calculated the field due to n current-loops, each bearing a current of $6e/n$, uniformly distributed on the toroidal surface; 24 such loops, distributed symmetrically between the upper- and lower tangent-tori, were found to be satisfactory.

On this basis, Farnum and Wilcox calculated the field for a three-

dimensional network of points in the vicinity of a hexagonal, benzenoid ring, exactly as Johnson and Bovey had done, and the results were finally expressed diagrammatically, as a 'correction', in ppm, which had to be added to the predictions of the Johnson-Bovey double-loop model, at each point in the network within the chosen volume. The calculated effect for all points further than $3 \text{ \AA}$ from the ring centre was substantially the same for both models; in particular, for points in the 'de-shielding' region, near the plane of the ring, such 'corrections' were very small — less than 0.05 ppm for the parts of this region accessible to proximate protons. In the 'shielding' region, however, above the plane of the ring, the differences between the predictions of the Waugh-Fessenden-Johnson-Bovey model and the Farnum-Wilcox approach can be as much as 0.3 ppm.

In the context of their refinements to the Waugh-Fessenden-Johnson-Bovey model, Farnum and Wilcox¹²⁶ emphasised the warning that classical models have the limitation of being "only a partial representation of a complete quantum-mechanical solution" and that, in general, "a refinement of a classical model does not guarantee that the new model will be a better representation of the actual molecular-situation". These authors successfully applied their model to the di- and tri-phenyl cyclopropenium ions. The present writer is not aware that they, or any other workers, have subsequently applied the method in other cases. The ready availability of the ubiquitous Johnson-Bovey tables¹¹⁸, and the small 'corrections' calculated for the 'deshielding' region, may furnish an explanation of this neglect.

(d) Classical Approaches Based on the Concept of Line Currents

In 1960, Longuet-Higgins and Salem^{127,20} discussed the chemical shifts in some annulenes by postulating that a line current (the magnitude of which had been calculated by a method based on the quantum-mechanical formalism of London³ (§1.4)) flowed around the perimeter

of the molecule, and that the contribution to the secondary magnetic-field, due to this line current, at the peripheral and inner protons, could be estimated classically from the Biot-Savart Law^{128,129}. An adaptation of this approach has recently been proposed by Haddon¹³⁰ who pointed out that the Biot-Savart-Law formalism using line currents has distinct advantages over the Waugh-Fessenden-Johnson-Bovey^{15,117} method when applied to annulenes, for the carbon skeletons of annulenes larger than benzene are very far from being circular. Furthermore, some of these molecules have a certain degree of non-planarity. Now extension of what is basically a π -electron theory to non-planar systems does, of course, require justification³⁸ (§1.4(i)(j)) but provided that the non-planarity is mild, the line-current approach has the flexibility to encompass this variant without any essential modification. In his application, Haddon¹³⁰ followed Waugh and Fessenden¹⁵ by adding the further requirement that the induced π -electron-currents do not flow through the atomic centres of the conjugated system but in current loops, the position of which is based on a least-squares minimisation of the differences between observed and calculated "ring-current" shifts. A further unique feature of Haddon's approach is that individual "ring-current" intensities are not calculated, or even assumed, but are, instead, deduced from a statistical comparison with experimental ¹H-NMR shifts.

In Chapter III of the present Thesis we shall be led quite naturally to a 'Biot-Savart' formalism for "ring-current" contributions to nuclear shielding in the process of developing an empirical theory of proton chemical-shifts for arbitrary conjugated-molecules without making appeal either to a 'test dipole' (§1.4 (i)(j)) or to the current-density operator (§1.4(ii)(b)). Presentation of the algebraical details underlying the Biot-Savart-Law formalisms will, therefore, be postponed until Chapter III.

1.4 Quantum-Mechanical Theories of the "Ring-Current" Effect

(i) The Hückel-London Method and its Extensions

(a) General Introduction

In 1937, London³ laid the foundations of the quantum-mechanical theory of π -electron "ring-currents" — an approach which was to receive only minor modification in the succeeding 25 years. In doing this, London was greatly inspired by the Bloch molecular-orbital theory of metals (as applied by Peierls¹⁰⁹ four years earlier) as well as by the pioneer work of Hückel¹¹⁵; for, in addition to having proposed the famous molecular-orbitals now known by his name, on which the London theory was originally based, Hückel was also one of several people who had earlier made the important qualitative suggestion that magnetic exhaltation in aromatic molecules might be due to the postulated mobilities of the π -electrons.

By introducing complex phase-factors into the atomic orbitals comprising the HMO's (these MO's being no longer purely real , in general, when the molecule is in the presence of an external magnetic-field), and by the device of constructing what are often termed 'gauge-invariant atomic-orbitals' (usually given the acronym 'GIAO'), London³ was able to give an explicit, and entirely quantum-mechanical, expression for the "ring-current" contribution to the magnetic susceptibility of a general, polycyclic, conjugated system. This expression had the further attractive feature that, for its application, knowledge was required only of the molecular geometry, and of the 'field-free' wave-function for the molecule — i.e. the (HMO) wave-function which describes the molecule in the absence of an external field.

The formalism proposed by London did not give the π -electron "ring-currents" per se — although (as will be seen in Chapter III) their intensities are, in fact, implicit in the calculated magnetic-anisotropies evaluated

by London's method; however, much later developments by Pople¹³¹ and McWeeny¹³² did give a procedure for calculating the magnetic moments associated with each individual ring (or, in the classical, Pauling terminology, the "ring currents") in a polycyclic molecule, these being quantities which are more useful, conceptually, in the context of NMR; it was, indeed, the advent of NMR in the mid-nineteen-fifties which provided the impetus for these extensions to the basic method of London.

Since the London theory is of such fundamental importance for nearly all that follows in this Thesis, we shall examine it in considerable detail. It has been reviewed previously on a number of occasions^{91,93,20,133,134} but our aim here is to give a uniform treatment of the Hückel-London method and of the various extensions and developments of it. This is done in order to emphasise that, within the confines of the Hückel-London approximations, the phenomena of magnetic anisotropy of (poly) cyclic, conjugated systems and the low-field chemical-shifts of their constituent protons, are merely two aspects of the way in which the entirely hypothetical "ring-currents" can be considered to manifest themselves, experimentally. Therefore, before we proceed to mathematical details, the reader is asked to bear in mind that the "ring currents" themselves are not physically observable; all that one can do is to postulate the model of π -electron "ring-currents" and then to calculate, on the basis of such a model, the resulting contributions to those quantities (such as magnetic anisotropies and ^1H -NMR chemical-shifts) which are experimentally measurable.

(b) The Effective, One-Electron Hamiltonian, $\mathcal{H}^{\text{eff}}$

Consider a planar, polycyclic, conjugated system, in the presence of an external magnetic-field which has a component B_0 along the z-axis, perpendicular to the molecular plane. The basic problem is to modify the secular equations arising out of a Hückel - type of Linear-Combination-of-Atomic-Orbital (LCAO)-scheme so that they are appropriate for describing

the molecule in the presence of this external magnetic-field.

In the presence of this constant component, $\vec{B}_0$, creating a vector potential $\vec{A}(j)$ at the j^{th} electron, the momentum of this electron is changed from $\vec{p}(j)$ to $(\vec{p}(j) + e\vec{A}(j))$; hence, the kinetic-energy operator for this particle becomes $\frac{1}{2m} (\vec{p}(j) + e\vec{A}(j))^2$, so that the one-electron Hamiltonian, $\mathcal{H}(j)$, is given by

$$\mathcal{H}(j) = \frac{1}{2m} (\vec{p}(j) + e\vec{A}(j))^2 + v(j) \quad (1.16)$$

where $\vec{p}(j) (= \frac{\hbar}{i} \vec{\nabla}_j)$ is the momentum operator for the j^{th} electron which is in a scalar potential $v(j)$, and in a magnetic field described by a vector potential $\vec{A}(j)$, due to the magnetic field $\vec{B}_0$, such that

$$\vec{B}_0 = \vec{\nabla}_j \times \vec{A}(j) \quad (1.17)$$

By invoking some vector identities, we can write this more explicitly as

$$\mathcal{H}(j) = \frac{\hbar^2}{2m} \nabla_j^2 + \frac{1}{2m} \left(\frac{\hbar e}{i} \vec{\nabla}_j \cdot \vec{A}(j) + \frac{2\hbar e}{i} \vec{A}(j) \cdot \vec{\nabla}_j + e^2 \vec{A}(j)^2 \right) + v(j) \quad (1.18)$$

When there is no magnetic field present, the Hamiltonian is invariant under operations which interchange like nuclei¹³⁵ (i.e., in terms of the coordinates (x_j, y_j, z_j) for the j^{th} particle, operations for which $v(x'_j, y'_j, z'_j) = v(x_j, y_j, z_j)$ when the transformation $x_j \rightarrow x'_j, y_j \rightarrow y'_j, z_j \rightarrow z'_j$ is effected). Such symmetry operations may not obtain, however, if a magnetic field is present. If the field, $\vec{B}_0$, is uniform, axes can be chosen appropriately (see later) such that¹³⁵

$$\vec{\nabla}_j \cdot \vec{A}(j) = 0$$

$$A(j)^2 = \frac{B_0^2}{4} (x_j^2 + y_j^2) = \frac{B_0^2}{4} (r_j^2 - z_j^2) \quad (1.19)$$

$$\begin{aligned} \vec{A}(j) \cdot \vec{\nabla}_j &= \frac{1}{2} B_0 (x_j \frac{\partial}{\partial y_j} - y_j \frac{\partial}{\partial x_j}) \\ &= \frac{1}{2} B_0 \frac{\partial}{\partial \phi_j} \end{aligned}$$

where, in the expressions on the r.h.s. of equations (1.19), we have changed to polar coordinates; these expressions then show that the only operation leaving the field-dependent part of the one-electron Hamiltonian invariant is a rotation, of arbitrary magnitude, about the field direction¹³⁵. An important consequence of this is that two states exhibiting (symmetry) degeneracy in the absence of the external field, will, in its presence, be separated, and give equal contributions to the magnetic susceptibility along the n-fold axis¹³⁵.

For an N-particle system, we then consider the sum of these separate Hamiltonians, to give (remembering, from equation (1.19), that $\vec{\nabla} \cdot \vec{A}(j) = 0$)

$$\begin{aligned} \mathcal{H} &= \sum_{j=1}^N \mathcal{H}(j) \\ &= \frac{-\hbar^2}{2m} \sum_{j=1}^N \nabla_j^2 + \frac{e\hbar}{im} \sum_{j=1}^N \vec{A}_j \cdot \vec{\nabla}_j \\ &\quad + \frac{e^2}{2m} \sum_{j=1}^N A_j^2 + \sum_{j=1}^N v(j) \end{aligned} \quad (1.20)$$

Denoting $\sum_{j=1}^N v(j)$ by V , the general, averaged, one-electron potential envisaged in the Hückel approximation, we can write equation (1.20) as^{133,136}

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2 \quad (1.21)$$

in which

$$\begin{aligned} \mathcal{H}_0 &= \frac{-\hbar^2}{2m} \sum_{j=1}^N \nabla_j^2 + V \\ \mathcal{H}_1 &= \frac{e\hbar}{im} \sum_{j=1}^N \underline{A}_j \cdot \underline{\nabla}_j \end{aligned} \quad (1.22)$$

and

$$\mathcal{H}_2 = \frac{e^2}{2m} \sum_{j=1}^N A_j^2$$

When the Hamiltonian for an N - particle system, $\mathcal{H}$, is written in this way, it can be seen that the eigenfunctions of $\mathcal{H}_0$ will be the eigenfunctions of the system in the absence of the external field, whilst the terms $\mathcal{H}_1$ and $\mathcal{H}_2$ may be regarded as perturbations introduced by the presence of this field. It is evident, furthermore, from the form of $\mathcal{H}_1$, that the eigenfunctions of this total π -electron Hamiltonian will no longer be purely real.

For the purposes of the London theory³, attention is directed to finding the eigenfunctions, ψ_i , and eigenvalues, ϵ_i , of the effective, one-electron Hamiltonian

$$\mathcal{H}^{\text{eff}}(j) = \frac{1}{2m} \left[(\underline{p}(j) + e\underline{A}(j))^2 \right] + V \quad (1.23),$$

where, henceforth, we shall drop the reference to 'j', simply writing

$$\mathcal{H}^{\text{eff}} = \frac{1}{2m} (\underline{p} + e \underline{A})^2 + V \quad (1.24)$$

it being understood that $\mathcal{H}^{\text{eff}}$ is a one-electron operator.

(c) 'Gauge-Invariance' Problems

So far in this discussion, we have avoided mention of one fundamental problem associated with the use of equation (1.17) as a 'definition' of $\underline{A}(j)$, the vector potential at electron j due to the external field; for what is actually being applied to the conjugated system is the external magnetic field $\underline{B}_0$, whereas in equations (1.16) - (1.24), and in the discussion concerning them, this magnetic field has been considered to manifest itself in the Hamiltonian (equation (1.18)) as a vector potential, $\underline{A}(j)$, at the j^{th} electron, 'defined' by equation (1.17). Unfortunately, however, (as has been much discussed - e.g. refs. 20, 133, 134) the vector potential $\underline{A}(j)$ is not determined uniquely once the external magnetic-field $\underline{B}_0$ has been specified. For, (again omitting reference to '(j)'), if

$$\underline{B}_0 = \nabla \times \underline{A} \quad (1.25)$$

then the gradient of any scalar function (ξ) can be added to $\underline{A}$, and, because the curl of the gradient of a scalar is zero, the same derived magnetic-field will result*. Hence

* The arbitrariness of $\underline{A}$ should not, of course, be surprising, since $\underline{B}_0$ is related to $\underline{A}$ by the curl operation of equation (1.25), which implies that the components of $\underline{B}_0$ are related to those of $\underline{A}$ by a series of three first-order, partial, differential equations (one for each component)

$$\begin{aligned} B_{0x} &= \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \\ B_{0y} &= \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \\ B_{0z} &= \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \end{aligned}$$

each of which therefore requires an arbitrary constant — conveniently regarded as the appropriate component of the gradient of some arbitrary scalar-quantity ξ .

$$\begin{aligned}
\underline{\nabla} \times (\underline{A} + \underline{\nabla} \xi) &= \underline{\nabla} \times \underline{A} + \underline{\nabla} \times \underline{\nabla} \xi \\
&= \underline{\nabla} \times \underline{A} \\
&= \underline{B}_0
\end{aligned}
\tag{1.26}$$

(by equation (1.25))

Furthermore, it can be shown¹³³ by simple substitution, and use of equation (1.24), that if Ψ is a solution to the equation

$$\mathcal{H}^{\text{eff}} \Psi = \epsilon \Psi \tag{1.27}$$

for a choice of $\underline{A}$ as vector potential, then Ψ' , defined

$$\Psi' = \Psi \exp \left(- \frac{ie}{\hbar} \xi \right), \tag{1.28}$$

is a solution to equation (1.27) with $(\underline{A} + \underline{\nabla} \xi)$ as a vector potential.

Now, a change of gauge can be as simple an operation as a mere change of origin; such a change would, however, evidently modify our effective, one-electron Hamiltonian (equation (1.24)) and so, in order to obtain the same eigenvalues from equation (1.27) — for, of course, in changing the origin, no change is made to the observable physical-properties of the system — it is clear that different eigenfunctions would have to be used. This is inconvenient, and the aim is to find unique wave-functions which are invariant to this change of gauge; such are the so-called 'gauge-invariant' molecular-orbitals.

To construct these, London assumed that the required gauge-invariant molecular-orbitals for the π -electrons of the system could be represented as a linear combination of GIAO's, such that if $\Psi_J^{(0)}$, the J^{th} MO in the absence of the field, is constituted from a linear combination of atomic orbitals $\{\phi_i^{(0)}\}$, then, in the presence of the field, the corresponding MO is:

$$\Psi_j = \sum_i c_{ij} \phi_i \quad (1.29)$$

where, by analogy with equation (1.28), $\{\phi_i\}$, in which

$$\phi_i = \phi_i^{(o)} \exp \left[\frac{-ie}{\hbar} \underline{A}_i \cdot \underline{r} \right], \quad (1.30)$$

is a set of atomic orbitals which will satisfy the required condition of gauge invariance (in the sense in which this term has been used previously in the present discussion). Here, $\phi_i^{(o)}$ is the i^{th} zero-field AO having, for most conjugated systems, approximately the form of an atomic $2p_z$ -orbital centred on the i^{th} nucleus of the system¹³², although it is assumed here that the set is orthonormal; more realistically (and committing ourselves less firmly) we describe it simply as the i^{th} basis-function in a Hückel LCAO-scheme; $\underline{A}_i$ in (1.30) is the vector potential, referred to an arbitrary origin, at the i^{th} nucleus of the system^{*}; also, in equation (1.30), $\underline{r}$ is the position vector of an electron in ϕ_i . Note that $\underline{A}_i \cdot \underline{r}$ in the exponent of equation (1.30) is, of course, a scalar quantity. (Let us call it $\xi(\underline{r})$, since it depends on the position of the electron in ϕ_i); equation (1.30) is, therefore, somewhat analogous to equation (1.28). Just as, therefore, it could be shown by direct substitution that Ψ' of equation (1.28) satisfied (1.27) for a vector potential $\underline{A} + \nabla \xi$, so, here, by taking ϕ_i defined in equation (1.30) and operating on it with $(\underline{p} + e \underline{A})^2$, it can be shown¹³³ that

* Note a potential source of confusion, extant in many accounts; $\underline{A}_i$ here refers to the vector potential at a nucleus of the conjugated system (in this case, the i^{th} nucleus) whereas $\underline{A}(j)$, referred to earlier (equations (1.16), (1.17) et seq.), denotes the vector potential at electron j ; and by $\underline{A}$ (unadorned) is also implied the vector potential at the position of the electron involved in the single-particle, effective Hamiltonian, as in equation (1.24).

$$(\tilde{p} + e \tilde{A})^2 \phi_i = \exp \left[\frac{-ei}{\hbar} \tilde{A}_i \cdot \tilde{r} \right] \{ \tilde{p} + e (\tilde{A} - \tilde{A}_i) \} \phi_i^{(0)} \quad (1.31)$$

It is thus seen that the GIAO's depend only on the local vector-potential, $\tilde{A} - \tilde{A}_i$, which is zero at the centre of atom i . This quantity represents the vector potential at the electron in ϕ_i ($\tilde{A}$, measured from an arbitrary origin) relative to that ($\tilde{A}_i$, measured from the same arbitrary origin) at the nucleus (i) of the conjugated system on which the AO ϕ_i is centred; $(\tilde{A} - \tilde{A}_i)$ is, therefore, independent of the arbitrary origin selected. It is thus evident^{20,133} that equation (1.31) shows that the gauge-dependent Hamiltonian (equation (1.24)), operating on the orbitals ϕ_i (equation (1.30)), is equivalent to the action on the zero-field AO's, $\phi_i^{(0)}$, of an operator which is effectively invariant to a change of gauge²⁰; and also that the GIAO's ($\{\phi_i\}$ — equation (1.30)) will form an appropriate basis for an LCAO-expression since, if $\phi_i^{(0)}$ is a solution to the Schrödinger equation in the absence of a magnetic field, ϕ_i is an approximate solution in the presence of such a field. The MO's Ψ_J (equation (1.29)) may thus be regarded as being 'gauge invariant' in the sense described. Note, however, that the term 'gauge-invariant orbitals' is something of a mis-nomer since, (as is clear from equation (1.30)), the orbitals per se are manifestly not invariant to a change of gauge — indeed, if they were, they would not perform their intended function of ensuring that the observable physical-properties of the system (such as the eigenvalues of the modified Hamiltonian (equation (1.23))) remain invariant to such changes. As Epstein¹³⁷ has pointed out, therefore, the MO's defined by equations (1.29) and (1.30) are perhaps more appropriately called 'gauge-variant' MO's; however, having drawn the reader's attention to this distinction, we continue to use the term 'gauge-invariant orbitals', as a concession to common usage, on the understanding that the above reservations are to be kept in mind.

(d) The Matrix Elements of $\mathcal{H}^{\text{eff}}$

If $\underline{k}$ is a unit vector perpendicular to the molecular plane, then

$$\underline{B}_0 = B_0 \underline{k} \quad (1.32)$$

and we may define

$$\underline{A} = \frac{1}{2} B_0 \times \underline{r} \quad (1.33)$$

where $\underline{r}$ is the position vector of an electron referred to an arbitrary origin. It will be noted that the form of equation (1.33) satisfies both the conditions that $\text{Curl } \underline{A} = \underline{B}_0$ (equation (1.25)) and that $\text{Div } \underline{A} = 0$ (equation (1.19)). At the i^{th} nucleus of the conjugated system, furthermore, if $\underline{R}_i$ is the vector relating this nucleus to the same, arbitrary origin,

$$\underline{A}_i = \frac{1}{2} B_0 \times \underline{R}_i \quad (1.34)$$

Now, from the general variation-method, by use of the GIAO-scheme specified in equations (1.29) and (1.30), the eigenvalues and the coefficients, c_{ij} , of equation (1.29) are derived from the secular equation

$$\left| \mathcal{H}^{\text{eff}} - E \mathcal{S} \right| = 0 \quad (1.35)$$

the matrix elements of which are calculated with the modified Hamiltonian, (equations (1.24) and (1.31)), giving

$$\begin{aligned} H_{ij}^{\text{eff}} &= \int \phi_i^* \mathcal{H}^{\text{eff}} \phi_j d\tau \\ &= \int \left\{ \exp \left[-\frac{ie}{\hbar} \underline{A}_i \cdot \underline{r} \right]^* \phi_i^{(0)} \left[\frac{1}{2} m(\underline{p} + e(\underline{A} - \underline{A}_j))^2 + v \right] \right. \\ &\quad \left. \phi_j^{(0)} \exp \left[-\frac{ie}{\hbar} \underline{A}_j \cdot \underline{r} \right] \right\} d\tau \end{aligned} \quad (1.36)$$

i.e.

$$H_{ij}^{\text{eff}} = \int \left\{ \exp \left[\frac{ie}{\hbar} (\underline{A}_i - \underline{A}_j) \cdot \underline{r} \right] \times \phi_i^{(0)*} \left[\frac{1}{2m} (\underline{p} + e(\underline{A}_i - \underline{A}_j))^2 + V \right] \phi_j^{(0)} \right\} d\tau \quad (1.37)$$

Furthermore, the overlap integral is

$$S_{ij} = \int \left\{ \exp \left[\frac{ie}{\hbar} (\underline{A}_i - \underline{A}_j) \cdot \underline{r} \right] \phi_i^* \phi_j \right\} d\tau \quad (1.38)$$

(e) The London Approximations

At this stage, London³ (and, later, Pople¹³¹) made the fundamental (and, in practice, the most drastic) assumptions of the theory, in order to reduce the matrix elements in equation (1.37) to an easily calculable form, simply related to the corresponding matrix-elements in the absence of the applied field.

1) If $i = j$, the exponential factor in equation (1.37) is unity, and the rest of the expression can be taken to be a measure of what Pople describes as "the basic energy of the AO, as modified by the local diamagnetic-circulation represented by the term $(\underline{A}_i - \underline{A}_j)$." Because this is supposed to be a theory about 'inter-atomic currents', the allegedly 'local' terms should not concern us. London and Pople therefore chose to neglect the contribution of $e(\underline{A}_i - \underline{A}_j)$ when i and j are bonded atoms; (when i and j are not bonded, H_{ij}^{eff} is neglected anyway—see assumption 3)). In so doing, it is also chosen that all H_{ii}^{eff} ($= \alpha$) are zero.

2) The off-diagonal elements, H_{ij}^{eff} , between AO's centred on atoms which are 'directly bonded' are, in general, modified by the exponential factor to be found inside the integral sign in equation (1.37). The major source of difficulty is the factor r , which denotes the position vector of an electron (integration being over all coordinates, τ , of this electron);

accordingly, the most famous (not to say infamous!) of the so-called "London approximations" was to assume that $\tilde{r}$ can be replaced by the value that it would have at the mid-point of the bond $i-j$, that is to say,

$$\tilde{r} = \frac{1}{2} (\tilde{R}_i + \tilde{R}_j) \quad (1.39),$$

R_i and R_j being the position vectors of the atoms labelled i and j in the conjugated system. The assumption is customarily justified (or, more correctly, rationalised) by alleging that the mid-point between the nuclei i and j will be close to what Pople describes as the "centre of overlap-distribution ϕ_i, ϕ_j ." It is not immediately obvious, however, that, even conceding this "centre-of-overlap-distribution" argument, we should consider such a centre to be at the mid-point of the $i - j$ bond in the molecular plane; rather, recalling the arguments of Johnson and Bovey and Waugh and Fessenden (§1.3(e)(ii)), we might expect the $2p_z$ - "maximum-overlap-distribution" to be at points above and below the centre of the bond $i - j$. However, as it turns out, within the spirit of the approximation, it is appropriate to consider the vectors $\tilde{R}_i$ and $\tilde{R}_j$ in the molecular plane^{*†}

The whole raison d'être of this approximation is, however, the vastly simplifying feature which it introduces — namely, that the exponential factor, which is now constant for a given i and j , can be taken outside the integral sign in equations (1.37) and (1.38). This, together with approximation 1) concerning the terms involving $(\tilde{A} - \tilde{A}_j)$, effectively

* For convenience and simplicity (and as a concession to tradition) the arbitrary (but subsequently fixed) origin, O , to which position vectors of the nuclei and electrons are referred, is here taken to be in the molecular plane. Such a requirement is, however, not necessary^{111,38} and indeed this restriction must be relaxed when discussing "ring-current" shielding-effects at points outside the molecular plane of a planar molecule¹³⁸, and when all "ring-current" effects in non-planar systems³⁸ are considered.

† This statement is proved in Appendix C of ref. 111.

reduces equations (1.37) and (1.38) to (1.40) and (1.41),

$$\text{i.e., } H_{ij}^{\text{eff}} = \left\{ \exp \left(\frac{ie}{2\hbar} (\tilde{A}_i - \tilde{A}_j) \cdot (\tilde{R}_i + \tilde{R}_j) \right) \right\} \times$$

$$\int \phi_i^{(0)*} \left[\frac{p^2}{2m} + V \right] \phi_j^{(0)} d\tau \quad (1.40)$$

and

$$S_{ij} = \left\{ \exp \left(\frac{ie}{2\hbar} (\tilde{A}_i - \tilde{A}_j) \cdot (\tilde{R}_i + \tilde{R}_j) \right) \right\} \times$$

$$\int \phi_i^{(0)*} \phi_j^{(0)} d\tau. \quad (1.41)$$

In equation (1.40), the quantity

$$\int \phi_i^{(0)*} \left[\frac{p^2}{2m} + V \right] \phi_j^{(0)} d\tau$$

is just $\beta_{ij}^{(0)}$, the ordinary resonance-integral of the non-magnetic Hückel-theory, and so

$$H_{ij}^{\text{eff}} = \beta_{ij}^{(0)} \exp \left\{ \frac{ie}{2\hbar} (\tilde{A}_i - \tilde{A}_j) \cdot (\tilde{R}_i + \tilde{R}_j) \right\}. \quad (1.42)$$

It is also clear that

$$(H_{ij}^{\text{eff}}) = (H_{ji}^{\text{eff}})^* \quad (1.43)$$

and so the elements H_{ij}^{eff} form an Hermitian matrix, guaranteeing the provision of real eigenvalues (as is required) even though the wave function itself (equations (1.29) and (1.30)) is, in general, complex, when the conjugated system is in the presence of the magnetic field.

In a similar (and obvious) notation, the overlap integral between nuclei i and j (S_{ij} —equation (1.41)) becomes

$$S_{ij} = S_{ij}^{(0)} \exp\left\{\frac{ie}{2\hbar} (\underline{A}_i - \underline{A}_j) \cdot (\underline{R}_i + \underline{R}_j)\right\} \quad (1.44)$$

Equations (1.43) and (1.44) illustrate a very clever (one might even say 'devious') feature of the London theory, which the approximations we have invoked in developing the argument have, by stealth, gradually brought about; it starts off by purporting to be a theory about how the external magnetic-field affects the momentum operators of the electrons in the π -orbitals of a conjugated system (e.g. equation (1.16)) but, by the time all the various approximations have been implemented (and in particular, of course, the so-called 'London' ones, just dealt with), all the formulae for the various matrix-elements and overlap-integrals depend only on the vector potentials which the external field creates at the nuclei of the polycyclic system, with no explicit mention of the field's effect on the π -electrons at all! Since the nuclei of the system (unlike the electrons) are assumed fixed, the simplifications which such a state of affairs creates are manifest—so much so, in fact, that, as we shall see, in order to calculate a "ring current", a magnetic anisotropy, or a chemical shift, on the basis of the simple London-theory, no actual integrals, as such, have explicitly to be evaluated!

It can be shown by vector geometry that the quantity

$$(\underline{A}_i - \underline{A}_j) \cdot (\underline{R}_i + \underline{R}_j) = 2S_{ij} B_0, \quad (1.45)$$

where S_{ij} is the signed (algebraic) area of the triangle formed by the origin (at which $\underline{A} = 0$) and the bond $i \rightarrow j$ of the conjugated network, counted positive if $i \rightarrow j$ is right-handed about the normal, $\underline{k}$, and

negative otherwise. It will be recalled that B_0 is the magnitude of the component of the external magnetic-field perpendicular to the molecular plane and it is, therefore, of some conceptual importance to realise that the quantity $S_{ij} B_0$ on the r.h.s. of equation (1.45) is proportional to the magnetic flux through the triangle Oij . Hence, equation (1.42) can be written

$$\begin{aligned} H_{ij}^{\text{eff}} &= \beta_{ij}^{(0)} \exp \left\{ \left(\frac{ie}{h} \right) S_{ij} B_0 \right\} \\ &= \beta_{ij}^{(0)} \exp \{ 2\pi i f_{ij} \} \\ (\text{i.e. } f_{ij} &= \left(\frac{e}{h} \right) S_{ij} B_0) \end{aligned} \quad (1.46)$$

3) Finally, since the London-Pople theory is based on an HMO-formalism, it is convenient to make several other assumptions which are within the spirit of the Hückel approximation

$$\text{i)} \quad \beta_{ij}^{(0)} = \beta^{(0)} \quad (1.47)$$

if there is a σ -bond between atoms i and j of the conjugation network,

ii) The Coulomb integral, α , is taken to be constant for all carbon-atoms and this integral is chosen as the energy zero. The binding energies, ϵ_J , in the presence of the magnetic field are therefore defined

$$\epsilon_J = E_J - \alpha \quad (1.48)$$

so that the quantity $(\alpha - \alpha^{(0)})$ is connected with the so-called 'local' contributions to the change in total energy, due to the presence of the external magnetic-field²⁰.

iii) The final Hückel-approximation is that overlap between even those atoms of the conjugated system which are adjacent (i.e. 'bonded'), is neglected — i.e.

$$\begin{aligned} \int \phi_i^* \phi_j d\tau &= \exp(2\pi i f_{ij}) \int \phi_i^{(0)*} \phi_j^{(0)} d\tau \\ &= \delta_{ij} \end{aligned} \quad (1.49)$$

(f) The Secular Determinant in the Presence of the Magnetic Field and the Quantum-Mechanical Concept of "Ring Currents".

With all these approximations, and with energies expressed relative to α and in units of $\beta^{(0)}$ (i.e., $x = \frac{E-\alpha}{\beta^{(0)}}$), the form of the Hückel secular-determinant appropriate for describing the molecule in the presence of the external magnetic-field is¹³¹

$$\left| \frac{1}{\beta^{(0)}} H_{ij}^{\text{eff}} - x \delta_{ij} \right| = 0. \quad (1.50)$$

The secular equation allowing calculation of the energies of the π -electrons in a magnetic field B_0 perpendicular to the molecular plane is thus obtained from the corresponding 'field-free' Hückel secular-determinant simply by replacing off-diagonal, real $\beta_{ij}^{(0)}$ -terms by the corresponding complex-conjugate elements $\beta_{ij}^{(0)} \exp(2\pi i f_{ij})$ and $\beta_{ji}^{(0)} \exp(-2\pi i f_{ij})$ (since, of course, $f_{ij} = -f_{ji}$ because of the relation $S_{ij} = -S_{ji}$).

It is convenient to discuss the general expansion of the secular determinant in terms of Tschebyscheff polynomials of the second kind⁹¹; these are defined by

$$x = 2 \cos \theta$$

$$T_n(x) = \frac{\sin \{(n+1) \theta\}}{\sin \theta} \quad (1.51)$$

i.e. $T_0 = 1$, $T_1 = x$, $T_2 = x^2 - 1$, etc. Let us consider initially the case of a linear chain of n carbon-atoms, the atoms being numbered sequentially along the chain. With

$$\left. \begin{aligned} \exp 2\pi i f_{rs} &= \omega_{rs} \\ &= \omega_{sr}^* \end{aligned} \right\} \quad (1.52)$$

(since $f_{rs} = -f_{sr}$)

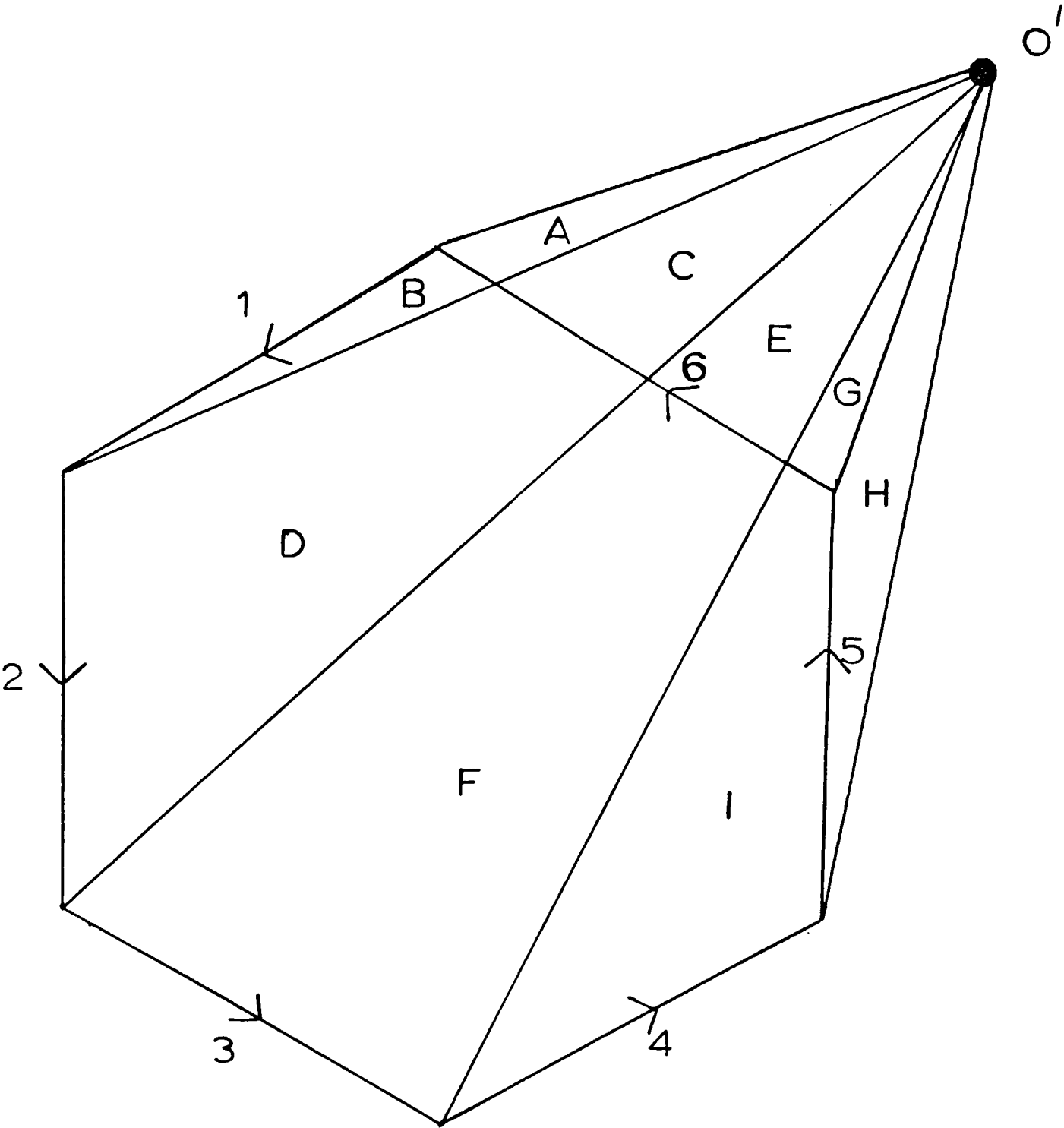
the secular equation (1.50) then becomes

$$D_n(x) = \begin{vmatrix} -x & \omega_{12} & 0 & 0 & . & . & 0 \\ \omega_{21} & -x & \omega_{23} & 0 & & & 0 \\ 0 & \omega_{32} & -x & \omega_{34} & & & 0 \\ & & & & \omega_{n-1,n-2} & -x & \omega_{n-1,n} \\ 0 & 0 & 0 & 0 & . & . & . \\ & & & & \omega_{n,n-1} & -x & \end{vmatrix} = 0 \quad (1.53)$$

Since, in every case, $\omega_{rs} \omega_{sr}^* = \omega_{rs} \omega_{rs}^* = 1$, the expansion of this determinant is just the Tschebyscheff polynomial $T_n(x)$ —the eigenvalues and eigenvectors of the matrix thus being independent of any external magnetic-field. If, however, we take a cyclic chain of n atoms, with the n vertices numbered sequentially around the ring, the secular determinant is as equation (1.53), above, except that the (1,n)- and (n,1)-elements are no longer zero, as they are in equation (1.53), but are now ω_{1n} and $\omega_{n1}^* (= \omega_{1n}^*)$, respectively.

The expansion of this determinant can then be written, in terms of Tschebyscheff polynomials, as⁹¹:

FIGURE 1.2



$\sum_{(ij)} s_{ij}$ Ordered Sum around
an irregular Hexagon.

$$\begin{aligned}
D_n(x) &= T_n - T_{n-2} + (-1)^{n-1} \omega_{12} \omega_{23} \cdots \omega_{nl} + (-1)^{n-1} \omega_{21} \omega_{32} \cdots \omega_{1n} \\
&= T_n - T_{n-2} + (-1)^{n-1} \exp [2\pi i (f_{12} + f_{23} + \cdots f_{nl})] \\
&\quad + (-1)^{n-1} \exp [-2\pi i (f_{12} + f_{23} + \cdots f_{nl})] \\
&= T_n - T_{n-2} + (-1)^{n-1} 2 \cos [2\pi (f_{12} + f_{23} \cdots f_{nl})]. \tag{1.54}
\end{aligned}$$

But

$$f_{12} + f_{23} + \cdots f_{nl} = \left(\frac{e}{h}\right) B_o (S_{12} + S_{23} + \cdots S_{nl}) \tag{1.55}$$

and $(S_{12} + S_{23} + \cdots S_{nl})$ is seen to be an ordered sum around the circuit enclosed by atoms 1 to n; the sum is, therefore, the area of the circuit enclosed by these atoms. This can be appreciated in the case of, say, a benzene hexagon (see Appendix E of ref. 111) by consideration of Figure 1.2, where the letters denote the moduli of the area segments indicated, and the summation is performed around the ring in the direction indicated by the arrows.

$$\begin{aligned}
\sum_{\substack{\text{(Bonds)} \\ (ij)}} S_{ij} &= (A+B) + (C+D) + (F+E) + (I+H+G) - H - (A+C+E+G) \\
&= B + D + F + I \\
&= |\text{Area of the hexagon}| \tag{1.56}
\end{aligned}$$

This result is quite general and continues to hold when the hexagon (or other such circuit) is not a regular figure (it must, however, be planar, and the point O' must be in its plane). It is also evident that the result holds wherever O' is chosen to be, in this plane; hence, the roots of

$D_n(x)$ are also independent of this choice. It is now clear that the quantity $(f_{12} + f_{23} + \dots f_{n1})$ is proportional to the magnetic flux through the polygon enclosed by the atoms 1 to n and that, in the London treatment, the external magnetic-field is brought into the problem by means of such 'ring' fluxes. It is also seen immediately that if the molecule contained no 'closed loops' (i.e. if, for example, it were a linear polyene) then all such $(f_{12} + f_{23} + \dots)$ -quantities would be zero, and hence all exponential terms in equation (1.54) would be unity; and $D_n(x)$ in equation (1.54) would revert to its 'field-free' form—that is to say, it would reduce to something like the 'linear-polyene' example we considered initially in equation (1.53). Evidently, therefore, without such circuits of atoms in the conjugated system, the external field has no effect in exciting "ring currents". This is, therefore, the quantum-mechanical 'justification' for the concept of "ring currents". An analogous (though formally different) justification (again within the context and assumptions of the London model) will be encountered later (§1.4) when the McWeeny theory¹³² is discussed.

In the case of a general, polycyclic molecule, each term in the expansion of $D(x)$ will be of the form⁹¹

$$\omega_{1r} \omega_{2s} \omega_{3t} \omega_{4u} \omega_{5v} \dots, \quad (1.57)$$

$r, s, t, u, v, \dots$ being any permutation of the indices $1, 2, 3 \dots$

Of course, the only non-zero ω_{ij} -terms are those which correspond to σ -bonds in the conjugated system, and so the non-zero terms of $D(x)$ such as (1.57) will be those⁹¹ which represent a closed path,*

* In freely using intuitive terms such as 'vertices', 'chains', 'paths', 'closed paths', 'loops' and 'cycles', we are following the custom in this subject of (unconsciously) adopting, in a loose and ill-defined way, the terminology of mathematical graph theory. These concepts will be more rigorously defined in Chapter VI of this Thesis, when the graph-theoretical aspects of simple "ring-current" calculations will be systematically examined.

$r, s, t \dots$, passing once, and once only, through the (distinct) vertices $r, s, t \dots$. As in the case of the monocyclic system just considered, if r is different from 1, s from 2, 3 from t , etc., then terms in the expansion of $D(x)$ will be of the form⁹¹

$$\exp [2\pi i (f_{1r} + f_{2s} + f_{3t} + \dots)]$$

where, as before, $(f_{1r} + f_{2s} + f_{3t} + \dots) = f_{r,s,t \dots}$ is proportional to the area of the polygon enclosed by the atoms $r, s, t \dots$. Also as in the monocyclic case, there will be a complex-conjugate term corresponding to this, and the two combined therefore give

$$\begin{aligned} & 2 \cos [2\pi(f_{1r} + f_{2s} + f_{3t} + \dots)] \\ &= 2 \cos [2\pi f_{rst} \dots] \end{aligned} \quad (1.58)$$

which is real. All the other terms are also real (a property guaranteed anyway by the Hermitian nature of the secular determinant). For example, if $r = 1$, the term in equation (1.57) is⁹¹

$$\begin{aligned} & \omega_{11} \omega_{2s} \omega_{3t} \omega_{4u} \omega_{5v} \\ &= \omega_{2s} \omega_{3t} \omega_{4u} \omega_{5v} \end{aligned} \quad (1.59)$$

corresponding to the polygon $s, t, u \dots$

If $r = 2$, $s = 1$, this same term is

$$\begin{aligned} & (\omega_{12} \omega_{21}) \omega_{3t} \omega_{4u} \omega_{5v} \\ &= (\omega_{12} \omega_{12}^*) \omega_{3t} \omega_{4u} \omega_{5v}. \end{aligned} \quad (1.60)$$

This corresponds to the polygon $t, u, v \dots$ since, again, $\omega_{12} \omega_{21} = \omega_{12} \omega_{12}^* = 1$, a real quantity. This will always be the case, and, by

proceeding in this way, it can be shown⁹¹ that $D(x)$ may be expressed

$$D(x) = D^{(0)}(x) + D^{(1)}(x) 2 \cos 2\pi f_1 + D^{(2)}(x) 2 \cos 2\pi f_2 \\ + D^{(1,2)}(x) 2 \cos 2\pi (f_1 + f_2) + \dots \quad (1.61)$$

where the $D^{(n)}(x)$ are polynomials in x independent both of the external magnetic-fields and of the areas of polygons contained within the general, polycyclic, conjugated system under consideration; and f_i in equation (1.61) is defined as

$$f_i = \frac{e}{h} B_0 S_i \quad (1.62)$$

where S_i is the (algebraic) area of the i^{th} irreducible circuit (i.e., the i^{th} ring) contained within the general, polycyclic, conjugated system.

Although we have not actually proved it here, it can be shown⁹¹ that results similar to equations (1.61) and (1.62) continue to hold when the assumptions about equal Coulomb-integrals and equal resonance-integrals are relaxed.

In principle, therefore, by virtue of equations (1.61) and (1.62), the problem is solved, for setting $D(x) = 0$ gives the modified energies, $\{x_i\}$ (and hence $\{E_i\}$ since $x_i = \frac{E_i - \alpha}{\beta(0)}$), of the π -electrons of the conjugated system, in terms of the geometry of the system and the strength of the external magnetic-field. Once this is known, the total π -electron-energy in the presence of the external magnetic-field is

$$E^\pi = \sum_K v_K E_K, \quad (1.63)$$

where v_K is the occupation number of the orbital of energy E_K . Then, E^π can be expressed as a power series in B_0 :

$$E^\pi = E^\pi(0) - \frac{1}{2} \frac{\chi^\pi}{\mu_0} B_0^2 + \dots \quad (1.63a)$$

in which χ^π represents the molecular diamagnetic-susceptibility (i.e., the component of the susceptibility per molecule, arising from the π -electron "ring-currents"). From here on we consider only the molecular susceptibilities - see equation (1.2) on page 8.

(g) Calculation of Magnetic Susceptibilities and "Ring Currents" from the Roots of the Modified Secular-Determinant

We now consider general formulae^{20,91} for magnetic susceptibilities and "ring-current" intensities, in terms of the modified orbital-energies which are the roots of the secular determinant appropriate to the case of a conjugated system in the presence of an external magnetic-field.

Firstly, the induced moment opposing the field is given by

$$M^\pi = - \frac{\partial E^\pi}{\partial B_0}, \quad (1.64)$$

where E^π is given by equation (1.63). This can also be written

$$\begin{aligned} M^\pi &= - \sum_i \frac{\partial E^\pi}{\partial f_i} \frac{\partial f_i}{\partial B_0} \\ &= \sum_i M_i^\pi \end{aligned} \quad (1.65)$$

in which f_i is as defined in equation (1.62); M_i^π thus depends on the variation of magnetic flux through the i^{th} ring and is a measure of the contribution of this ring to the total induced-moment due to the 'mobile' π -electrons; and if M_i^π were considered to arise from an induced line-current, J_i , around the i^{th} ring, (see §1.3(iv) and Chapter III) then, classically,²⁰

$$M_i^\pi = J_i S_i \quad (1.66)$$

Therefore,
$$J_i = - \frac{e}{h} \frac{\partial E^\pi}{\partial f_i}. \quad (1.67)$$

Substitution for E^π from equation (1.63) gives

$$J_i = -\frac{e}{h} \sum_K v_K \frac{\partial E_K}{\partial f_i} \quad (1.68)$$

which, for a closed-shell system, can be written

$$J_i = -\frac{e}{h} 2 \sum_{K=1}^{\text{occ}} \frac{\partial E_K}{\partial f_i} \quad (1.69)$$

Thus, if we know the way in which the total orbital-energy changes with variation in the flux passing through the i^{th} ring of the conjugated system, then, by equations (1.66 - 1.69), we can, in principle, calculate what can be described as the "ring current" associated with that ring.

From equation (1.63a),

$$\begin{aligned} \chi^\pi &= -\mu_o \left(\frac{\partial^2 E^\pi}{\partial B_o^2} \right)_{B_o = 0} \\ &= -\mu_o \left[\frac{\partial}{\partial B_o} \left(\frac{\partial E^\pi}{\partial B_o} \right) \right]_{B_o = 0} \\ &= \mu_o \left(\frac{\partial M^\pi}{\partial B_o} \right)_{B_o = 0} . \end{aligned} \quad (1.70)$$

This can likewise be split into terms associated with each individual-ring, to give (by use of equations (1.65) - (1.67)):

$$\begin{aligned} \chi^\pi &= \sum_i \mu_o \left(\frac{\partial (J_i S_i)}{\partial B_o} \right)_{B_o = 0} \\ &= \mu_o \sum_i S_i \left(\frac{\partial J_i}{\partial B_o} \right)_{B_o = 0} . \end{aligned} \quad (1.71)$$

Since only terms linear in B_o are retained in the London method, this

is more conveniently written

$$\chi^{\pi} = \mu_0 \sum_i S_i J_i / B_0 \quad (1.72)$$

(rings)

It is clear, therefore, that there are two distinct ways of calculating the diamagnetic susceptibility of a conjugated system on the London model. Either this can be done directly from a knowledge of the roots of the modified secular-determinant, using equation (1.70) (this was the approach adopted by London³) or, the susceptibility can be obtained via an intermediate calculation of the π -electron "ring-currents" associated with each individual ring of the conjugated system in question—as in equation (1.72). This second route was apparently not deemed to be required for the calculation of magnetic susceptibilities (indeed, such a method was not available until 1958) and most of the numerical values reported in the Literature have been obtained without recourse to explicit evaluation of "ring-current" intensities. For the discussion of NMR chemical-shifts, on the other hand, it has customarily been found that to obtain explicit numerical-values for the individual "ring-currents" is helpful conceptually (even though, as will be seen in §1.4, such an intermediate calculation is also not actually necessary, for the evaluation of secondary magnetic-fields due to the 'mobile' π -electrons).

In the next two sub subsections we therefore examine two different (but equivalent) procedures for calculating (on the Hückel-London model) the numerical values of the "ring-current" intensities excited in a general, planar, polycyclic system by an external magnetic-field, in terms of

- i) the geometry of the molecule
- ii) the strength of the external field
- iii) the HMO-coefficients and energy-levels appropriate to the molecule in the absence of external magnetic-fields.

Both approaches, which are essentially extensions of the simple London-method based on HMO-theory,

were put forward in 1958, one by Pople¹³¹, and other by McWeeny¹³².

(h) Pople's Method

We begin by re-writing equation (1.61) in slightly-more convenient symbolism

$$\begin{aligned} P(x) (\equiv D(x) - D^{(0)}(x)) \\ = q_1(x) \cos 2\pi f_1 + q_2(x) \cos 2\pi f_2 \\ + q_{12}(x) \cos 2\pi (f_1 + f_2) + \dots \end{aligned} \quad (1.73)$$

Then, if the perturbation is small enough¹³³,

$$\cos 2\pi f_i = 1 - \frac{4\pi^2 f_i^2}{2} \quad (1.74)$$

and equation (1.73) can be written, after expansion in terms up to B_o^2 ,

$$P(x) = 4\pi^2 \sum_{i,j} Q_{ij}(x) f_i f_j \quad (1.75)$$

where $Q_{ij}(x)$ is a set of polynomials in x , and $P(x^{(0)})$ is the field-free secular-equation; in the absence of degeneracy, the solutions to second order are related to the zero-field solutions by

$$x_K = x_K^{(0)} + 4\pi^2 \sum_{ij} x_K^{ij} f_i f_j \quad (1.76)$$

Here, $x_K^{(0)}$ is the K^{th} solution of the unperturbed, ('field-free') secular-equation and¹³³

$$x_K^{ij} = \frac{Q_{ij}(x_K^{(0)})}{P'(x_K^{(0)})} \quad (1.77)$$

As is essentially done in the conventional London-method, the total change in energy due to the applied field B_o could be found by calculating

the f_i -terms, finding the change in each energy-level by equation (1.76), and then summing over all electrons in all occupied orbitals. The novel feature of Pople's treatment, however, was the introduction of a small, secondary, 'test' field, $\underline{B}^t$, in addition to the primary field, $\underline{B}_0$, as a device for finding how the total magnetic-moment induced by the external field, $\underline{B}_0$, is distributed amongst the various rings of the polycyclic system. The total magnetic-field is then $\underline{B}_0 + \underline{B}^t$, and so f_i becomes $f_i + f_i^t$, so that, approximately,

$$x_K = x_K^{(0)} + 4\pi^2 \sum_{ij} x_K^{ij} (f_i f_j + 2f_i^t f_j + f_i^t f_j^t). \quad (1.78)$$

Since f_i^t is proportional to the flux of $\underline{B}^t$ through the i^{th} ring, the term in $f_i^t f_j$ can be taken to represent the interaction of the test field with a current, J_i^K , in the i^{th} ring, due to the influence of $\underline{B}_0$ on the MO ψ_K . Classically, this current is equivalent to a dipole of strength

$$\underline{M}_i^K = J_i^K \underline{S}_i \quad (1.79)$$

and it has a potential energy of interaction with $\underline{B}^t$ of

$$\begin{aligned} E_{\text{mag}} &= - \underline{M}_i^K \cdot \underline{B}^t \\ &= J_i^K \underline{S}_i \cdot \underline{B}^t \\ &= J_i^K f_i^t \left(\frac{h}{e}\right). \end{aligned} \quad (1.80)$$

Comparison with the corresponding terms in the perturbed energy of the K^{th} MO (equation (1.78)) gives

$$J_i^K = \frac{8\pi^2 \beta^{(0)} e}{h} \sum_j x_K^{ij} f_j. \quad (1.81)$$

Summation of these 'partial' currents over all MO's, K, leads to

$$J_i = \sum_K v_K (8\pi^2 \beta^{(0)} (\frac{e}{h})^2) \times \sum_j x_K^{ij} (S_j B_o) \quad (1.82)$$

Furthermore, from equation (1.66) it can be seen that the magnetic energy is identical with that of a set of magnetic shells, one for each ring of the molecule, with strengths given by equations (1.66) and (1.82). The signs in equation (1.82) are such that in the case of the benzenoid molecules the effect is diamagnetic,¹³² and the magnetic shell for each ring may be formally associated with an induced current, J_i (equation (1.82)), circulating clock-wise about the applied field. Hence, one can formally calculate "ring currents" for each ring of a polycyclic molecule, from a knowledge of the Hückel-London secular-determinant.

(i) McWeeny's 'Test-Dipole' Polarisability-Method¹³²

The starting point for the McWeeny theory is equation (1.46) in which, from here on, we shall call H_{ij}^{eff} , β_{ij} . Like Pople, McWeeny introduced a point dipole, of moment $\underline{m} = m \underline{k}$, in order to probe the induced-current distribution in the molecule by calculating the coupling energy ($-\underline{m} \cdot \underline{B}'$) between $\underline{m}$ and the secondary magnetic-field, $\underline{B}'$, at the position of $\underline{m}$, due to this current distribution.* This test dipole is introduced at any point in the vicinity of the molecule at which it is required to calculate the secondary field due to the 'mobile' π -electrons. For convenience, this point is chosen to be in the molecular plane, though it need not necessarily be so (see §1.4(i)(j)). The vector potential at point $\underline{r}$ will then be

$$\underline{A} = \frac{1}{2} \underline{B}_o \times \underline{r} + \frac{m\mu_o}{4\pi} \frac{\underline{r} \times \underline{k}}{r^3} \quad (1.83)$$

The equivalent of equation (1.46) can then be written

* The legitimacy, or otherwise of this step is discussed in ref. 219, Chapter III and Appendix A.

$$\beta_{ij} = \beta_{ij}^{(o)} \exp\left\{2\pi i \frac{e}{h} S_{ij} \left(B_o + \frac{\mu_o m}{4\pi R_i^3} + \frac{\mu_o m}{4\pi R_j^3}\right)\right\} = \beta_{ij}^{(o)} \exp(i \theta_{ij}) \quad (1.84)$$

This may be further simplified to

$$\beta_{ij} = \eta_{ij} \beta^{(o)} \exp(i \theta_{ij}) \quad (1.85)$$

where $\beta^{(o)}$ ($=\beta$) is the standard carbon-carbon benzene resonance-integral of the non-magnetic Hückel-theory. Furthermore, for consistency and simplicity we shall here assume that all $\eta_{ij} = 1$; this assumption will be relaxed later (Chapter III). With respect to the zero-field AO's, the matrix elements of the perturbation due to the field are then

$$\begin{aligned} \Delta_{ij} &= \beta_{ij} - \beta^{(o)} \\ &= \beta^{(o)} - (e^{i\theta_{ij}} - 1) \\ &= \beta^{(o)} \left(i \theta_{ij} - \frac{1}{2} \theta_{ij}^2 + \dots \right) \end{aligned} \quad (1.86)$$

Then, by a rather involved double-perturbation argument (which is not reproduced here but full details of which are given in refs. 132-134 and 111) McWeeny showed that the total magnetic-energy in the presence of both the field B_o and the dipole $\underline{m}$ may be expressed as the sum of a first-order and a second-order term:

$$E^{\text{mag}} = E^{(a)} + E^{(b)} \quad (1.87)$$

With

$$E^{(a)} = -\beta \sum_{\substack{\text{bonds} \\ (ij)}} \theta_{ij}^2 P_{ij}$$

$$= -\beta \left(\frac{2\pi e}{h} \right)^2 S^2 \sum_{(ij)} P_{ij} s_{ij}^2 \left\{ B_o^2 + \frac{2B_o^m k_{ij}}{4\pi a^3} \mu_o + \dots \right\} \quad (1.88)$$

and

$$\begin{aligned} E^{(b)} &= - \sum_{\text{bonds } (ij)} \sum_{\text{bonds } (kl)} \beta \theta_{ij} \theta_{kl} \beta \bar{\pi}_{(ij)(kl)} \\ &= -\beta \left(\frac{2\pi e}{h} \right)^2 S^2 \sum_{(ij)} \sum_{(kl)} \beta \bar{\pi}_{(ij)(kl)} s_{ij} s_{kl} \\ &\quad \left\{ B_o^2 + \frac{2B_o^m}{4\pi a^3} \mu_o \left(\frac{k_{ij} + k_{kl}}{2} \right) + \dots \right\} \end{aligned} \quad (1.89)$$

In equations (1.85) and (1.86), S is the area of a standard benzene-hexagon, and s_{ij} is the previously defined signed-area, S_{ij} , of the triangle formed by the origin and the atoms at the extremities of the bond $i-j$, but now (more conveniently) expressed in units of S ;

$$k_{ij} = \frac{1}{r_i^3} + \frac{1}{r_j^3} \quad (1.90)$$

where R_i (the length of the vector relating the i^{th} nucleus of the conjugated system to the origin) = ar_i , a being the length of a standard carbon-carbon bond in benzene. P_{ij} is the ordinary, Coulson bond-order of the $i-j$ bond (calculated from the normalised eigenvectors of the field-free, Huckel Hamiltonian-matrix); and $\bar{\pi}_{(ij)(kl)}$ is what McWeeny called the mutual, imaginary, bond-bond polarisability of the bonds (ij) and (kl) .

This quantity (explicitly defined and discussed in Chapter VI and Appendix D, and in Chapter VII, of this Thesis) is the analogue, for complex perturbations (such as arise when a magnetic field is present), of the real, mutual, bond-bond polarisability, $\pi_{(ij)(kl)}$, defined by Coulson and

Longuet-Higgins¹³⁹. For, just as the real polarisability is given by

$$\pi_{(ij)(kl)} = \frac{1}{\beta} \frac{\partial P_{ij}}{\partial \beta_{kl}}, \quad (1.91)$$

so the imaginary bond-bond polarisability $\bar{\pi}_{(ij)(kl)}$ is the imaginary part of the change of bond order P_{ij} per unit change in imaginary part of resonance integral β_{kl} . Since this is a mutual polarisability, $\bar{\pi}_{(ij)(kl)} = \pi_{(kl)(ij)}$; (however, $\bar{\pi}_{(ij)(kl)} = -\bar{\pi}_{(ij)(lk)} = -\bar{\pi}_{(ji)(kl)}$ — see Appendix D). P_{ij} and $\bar{\pi}_{(ij)(kl)}$ are thus to be determined from ordinary, (non-magnetic) HMO-theory.

From equations (1.87) - (1.89) it is evident that if we were interested only in diamagnetic susceptibilities or (only) "ring-current" intensities (or, indeed, if the 'test' dipole were absent!) we would consider the coefficient of the term in B_o^2 , exactly as was done in the original London-method. (This is the initial procedure adopted in the analysis presented in Chapter III.) However, it is also seen from equations (1.87)-(1.89) that the total magnetic-energy in the presence of the field, B_o , and the dipole, m_k , differs from that with the dipole absent by the coupling term

$$\Delta E^{\text{dipole}} = - 2\beta \left(\frac{2\pi e}{h} \right)^2 \frac{S_o^2 B_o m}{4\pi a^3} (\sigma_1 + \sigma_2),$$

where

$$\sigma_1 = \sum_{\substack{\text{(bonds)} \\ (ij)}} P_{ij} s_{ij}^2 \quad (1.92)$$

$$\sigma_2 = \sum_{(ij)} \sum_{(kl)} \beta \bar{\pi}_{(ij)(kl)} s_{ij} s_{kl} \frac{(k_{ij} + k_{kl})}{2}$$

Since ΔE^{dipole} in equations (1.92) may be identified with $-\frac{m \cdot B}{\hbar}$,

where $B'_{\underline{m}}$ is the secondary magnetic-field at the origin (i.e. the position of $\underline{m}$) due to the mobile π -electrons, we obtain* (after further dividing by 3 in order to average over all random orientations of the molecule with respect to the fixed, external field B_0 — see Appendix A of ref. 111) the isotropic value of B' , which is

$$B' = \frac{2\beta}{3} \left(\frac{2\pi e}{h} \right)^2 \frac{S_{\mu_o}^2 B_o}{4\pi a^3} (\sigma_1 + \sigma_2) \quad (1.93)$$

By use of a clever unitary-transformation on the basis orbitals (which is fully described and discussed in Chapters III & VI of this Thesis) McWeeny was able to simplify this expression in order to cast it in the form

$$B' = \frac{2}{3} \beta \left(\frac{2\pi e}{h} \right)^2 \frac{S_{\mu_o}^2 B_o}{4\pi a^3} \sum_t J_t \left[-K(\underline{r}_t) \right], \quad (1.94)$$

where

$$K(\underline{r}_t) = \sum_{\substack{\text{around} \\ \text{ring } t}} s_{ij} k_{ij} \quad (1.95)$$

in which the sum is taken around the ring whose centre is related to the origin by the position vector $\underline{r}_t$. J_t is then identified with the "ring-current" intensity in the t^{th} ring of the arbitrary, conjugated system on which the calculation is being based. (An explicit expression for J_t will be presented in Chapter III). For a given external-field B_0 ,

* In c g s ('non-S I') units, this equation would be (eg. ref. 140)

$$H' = \frac{2}{3} \beta \left(\frac{2\pi e}{hc} \right)^2 \frac{S_{\mu_o}^2 H_o}{a^3} (\sigma_1 + \sigma_2) \quad (1.93a)$$

therefore, equation (1.94) is of the form

$$B' = \text{constant} \times \sum_t J_t \left[-K(\underline{r}_t) \right]. \quad (1.96)$$

J_t is calculated from HMO-quantities such as P_{ij} and $\overline{\pi}_{(ij)(kl)}$, together with a knowledge of the areas of the various rings in the molecule (See Chapters III and V). $K(\underline{r}_t)$ is a purely geometric factor which depends merely on the physical position in space of the origin in question, relative to the t^{th} ring; its magnitude is thus determined solely by molecular geometry and is a measure of the effect which the "ring current" in ring t of the molecule has on the secondary field at the point under test. In an $^1\text{H-NMR}$ experiment, this point might conveniently be chosen to be the position of a proton whose resonance is being investigated; the ratio B'/B_0 would then represent the contribution to the shielding of this proton, in a nuclear-magnetic-resonance experiment, from the "ring currents" in all the rings of an arbitrary, planar, polycyclic system. From the above outline, and from the discussion in Chapter III and elsewhere in this Thesis, the McWeeny method will eventually be seen to have the following attractive features:

- 1) If the dipole term is neglected the method provides an alternative, though entirely equivalent, approach to the original London one of calculating overall "ring-current" contributions to the magnetic susceptibilities of planar, conjugated systems. (This aspect is emphasised in the discussions in Chapter III).
- 2) Whether or not the dipole term is included the McWeeny formalism provides an alternative, though again entirely equivalent, method to Pople's for computing the explicit, relative, "ring-current" intensities in the various individual-rings of a planar, polycyclic, conjugated molecule. (See also an explicit expression presented in Chapter III).

3) When the dipole coupling-term is taken into account the McWeeny method affords a direct, and entirely quantum-mechanical, way (equations (1.93) and (1.94)) of determining the secondary magnetic-field at any point in space in the vicinity of a given planar, polycyclic, conjugated molecule, due to the "ring currents" in all rings of that molecule. It can thus be used directly to make predictions of how "ring currents" affect proton chemical-shifts in such molecules.

It is, however, important to observe that, if equation (1.93) is employed, rather than (1.94), the McWeeny formalism can yield these chemical shifts without the necessity for an intermediate calculation of individual "ring-current" intensities¹⁴¹. This point emphasises the fact (referred to on p. 24) that the individual "ring-current" intensities themselves are a conceptual convenience, rather than a physical observable. Furthermore, this direct accessibility of "ring-current" secondary-fields (and hence nuclear-shieldings) is an attribute of the McWeeny theory¹³² which is not shared, for example, with the semi-classical formalism reviewed in §1.3 (v) (a)-(c) and dealt with in Chapter II; all of these semi-classical methods require intermediate evaluation of individual "ring-currents", the effects of which are then assessed via a classical distribution-function, yielding geometrical factors dependent upon the geometry of the molecule and the position of the resonating nucleus under test — that is to say, these other methods are the analogy of equation (1.94) of the McWeeny formalism, rather than equation (1.93). *

* Historical note on the London-McWeeny method: In an unpublished document dated May 16th, 1953 (deposited in file no. B.38.6 of the Coulson Papers in the Contemporary Scientific Archives Collection of the Bodleian Library, University of Oxford) the present author's first supervisor, the late Professor C.A. Coulson, F.R.S., formulated the London theory of magnetic susceptibility in terms of his own 'contour-integral' approach (C.A. Coulson, Proc. Cambridge Philos. Soc., 36, 201 (1940)). The Coulson contour-integral formalism was much favoured by its originator, but, perhaps because of its rather esoteric nature, has been less generally and less enthusiastically adopted by other authors. In the above document, Coulson also advances an alternative approach, within

(j) Out-of-Plane Calculations: The Haigh-Mallion Tables

In the whole of the preceding discussion, we have assumed that a) the conjugated system under study is planar, and b) the origin, 0, at which the test dipole is placed in order to probe the "ring-current" secondary magnetic-field at 0, is in the molecular plane. Haigh and the present author^{38b,138} have investigated the repercussions for the London-McWeeny formalism which follow when all the quantum-mechanical approximations inherent in that theory are retained, but the above geometrical constraints are relaxed. This was done in order to be able to treat molecules such as the helicenes which, as was discussed in §1.2, have quite striking and interesting "ring-current" effects^{38,111}. Under these conditions, the magnitude of $\tilde{B}'$ is still given by equation (1.93) but, in place of equation (1.92) defining σ_1 and σ_2 , these authors substituted

$$\sigma_1 = \sum_{(ij)} P_{ij} (s_{ij}^{\text{plane}})^2 k_{ij}$$

$$\sigma_2 = \sum_{(ij)} \sum_{(kl)} \beta \pi_{(ij)(kl)} s_{ij}^{\text{plane}} s_{kl}^{\text{plane}} \left(\frac{k_{ij} + k_{kl}}{2} \right) \tilde{n}_{ij} \cdot \tilde{n}_{kl}$$
(1.96)

Since this theory is concerned with that part of the nuclear shielding arising from π -type orbitals, Haigh and Mallion included only that part of the vector potential arising from the component of the field (and test

*(Footnote continued from previous page)

the framework of

the HMO-method and the London approximations, for calculating overall magnetic-susceptibilities of conjugated molecules; the Coulson approach is also based on bond-bond polarisabilities and therefore provides an interesting parallel to certain aspects of the McWeeny polarisability-method¹³² just described in the text — although the Coulson polarisability-formalism, as presented, does not provide for explicit computation of individual "ring-current" intensities nor, of course, (since it preceeded the experimental observation^{5,6}!) for the direct calculation of "ring-current" secondary-fields (and hence ¹H-NMR chemical-shifts).

I am very grateful to Mrs. Eileen Coulson for her kindness in allowing my access to file B.38.6 before its deposition in the Bodleian Library.

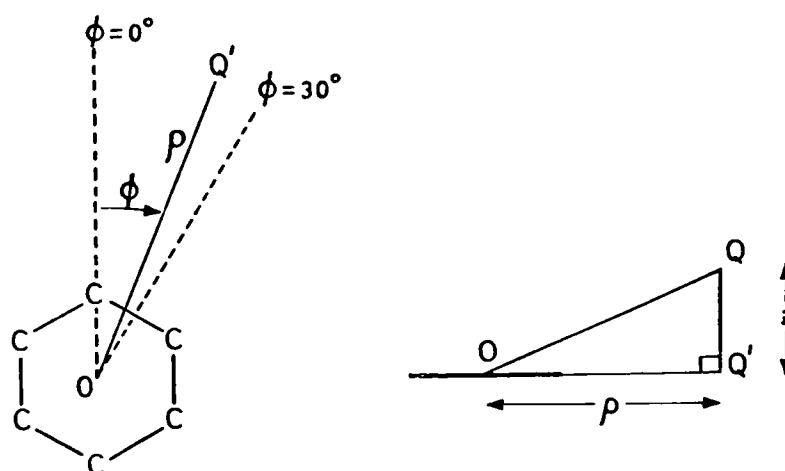
dipole) perpendicular to the π -electron nodal-plane. In a non-planar molecule this can no longer, of course, be a single plane; a best approximation is therefore chosen (see refs 38b and 111 for details) for each bond, $i-j$, and this is denoted by the ' $i-j$ bond-plane'. In equations (1.96), s_{ij}^{plane} is the signed area (in units of S) of the triangle $O'ij$ where O' is the projection of the origin, O , onto the $i-j$ bond-plane. $\hat{n}_{ij}$ and $\hat{n}_{kl}$ are unit vectors perpendicular to the planes of bonds ij and kl , respectively; the $\hat{n}_{ij} \cdot \hat{n}_{kl}$ -terms are, therefore, the cosines of the angles between pairs of bond planes. It should be noted that the transformation from equation (1.93) (with σ_1 and σ_2 defined in (1.96)) to the analogy of (1.94) involving a sum over rings, is not possible if the conjugated system is non-planar because equation (1.56) no longer holds.

This formulation, involving the concept of a bond plane, is applicable only if the skeletal distortion about any one bond is comparatively mild. Because of the way in which strains from overcrowding are spread over many degrees of freedom^{142,143}, this condition does appear to be satisfied in the case of the helicenes, even though the overall non-planarity between well-separated parts of such molecules may in fact be very large. As a result, Haigh and Mallion applied their formulation^{38b} with some success to rationalise the observed ^1H NMR chemical-shift patterns^{38a} in tetra-, penta- and hexahelicene.

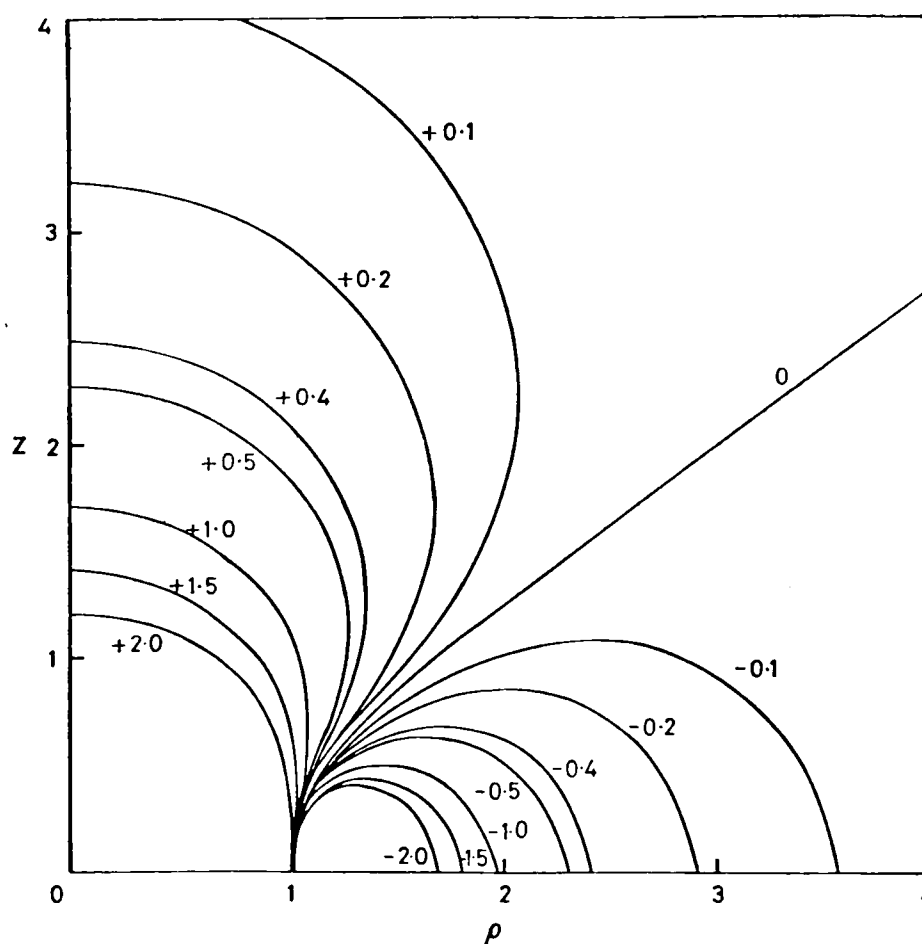
If we allow the relaxed assumption (b), above, but retain a planar skeleton for the conjugated system, all bond planes become identical with the molecular plane. Equation (1.96) is thus simplified since the last (angular) factor, $\hat{n}_{ij} \cdot \hat{n}_{kl}$, is identically unity. Accordingly, equations (1.93) and (1.96) now differ from the corresponding ones of the wholly-planar McWeeny-theory (equations (1.92) and (1.93)) only in the replacement of the signed-area terms by their projections onto the molecular plane. Because the equivalent of equation (1.56) (but now involv-

FIGURE 1.3

Coordinate System for, and Theoretical Predictions of, the Haigh-Mallion
Tables



(a) Cylindrical Polar-Coordinates Used



(b) Iso-Shielding Lines, from the Haigh-Mallion
Tables, for $\phi = 0^\circ$. Shieldings are in p.p.m.

ing projected areas) again holds, it is once more possible to use the analysis in the latter part of ref. 132 to obtain the simpler formula (1.94). The only difference is that $K(\underline{r}_t)$ in (1.94) (defined by (1.95)) is replaced by $K'(\underline{r}_t)$, defined

$$K'(\underline{r}_t) = \sum_{\substack{\text{around} \\ \text{ring } t}} (s_{ij}^{\text{plane}}) k_{ij} , \quad (1.97)$$

where the ordered sum is over bonds within the t^{th} ring. $K'(\underline{r}_t)$ in equation (1.97) thus differs from the corresponding term, $K(\underline{r}_t)$, in (1.95) merely by the use of projected signed-areas. This simplified formula (equations (1.94) and (1.97)) gives a measure of the intra- or inter-molecular "ring-current" effect of (say) a benzene ring on the chemical shift of a proton in any position relative to it — exactly as the classic (and classical) Johnson-Bovey tables^{117,118} do (discussed in §1.3 (v) (b)). Haigh and Mallion accordingly made available^{111,138} a set of "ring-current" shielding-tables similar in format and purpose to the earlier ones of Johnson and Bovey, but based on the semi-empirical, quantum-mechanical formalism summarised by equations (1.94) and (1.97). Because the quantum-mechanical theory takes account of the hexagonal symmetry of the benzene ring (unlike the classical theories which assume it to be circular), the new tables are based on the cylindrical polar-coordinates (ρ, ϕ, z) defined in Figure 1.3. Figure 1.3 shows 'iso-shielding lines' (i.e., sets of contours of constant shielding for different combinations of ρ and z) for a plane perpendicular to the molecular plane containing a line through one carbon atom and the ring centre (i.e., $\phi = 0$). This is of course similar in overall appearance to the corresponding diagram (Fig. 1 of ref. 117) of Johnson and Bovey; in both cases, the zero contour, which separates the lateral deshielding-region from the larger shielding-zone, quite quickly attains the limiting slope-

angle of $\sin^{-1} (1/\sqrt{3})$ appropriate to a classical dipole-field.

Some comments on, and comparisons between, the Johnson-Bovey tables and the Haigh-Mallion tables will be made in the next sub-sub-section.

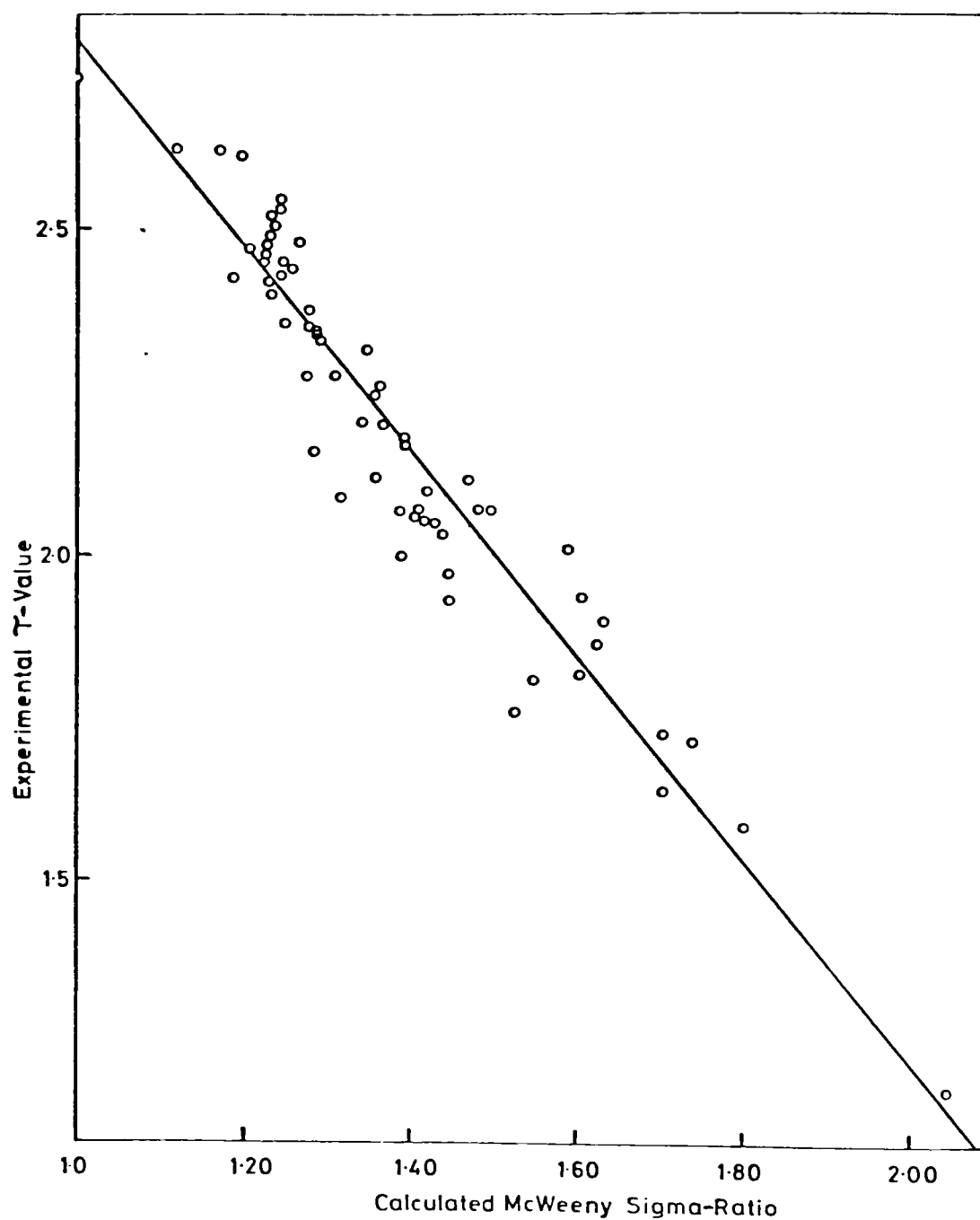
(k) Numerical Applications of the Hückel-London-McWeeny Method and its Extensions

The simple Hückel-London-Pople-McWeeny approach has been much applied to conjugated hydrocarbon-systems by a large number of authors over a long period, particularly to calculate $\chi_{\perp}^{\pi\text{London}}(\text{molecule})/\chi_{\perp}^{\pi\text{London}}(\text{benzene})$ ratios [see refs. 3, 135, 91, 93, 131, 132, 24, 120, 114, 122, 116, 111, 32, 33 and 144-161]. These ratios have then often been compared with experimental estimates of these quantities (a hazardous undertaking since London π -electron contribution alone, unscrambled from other contributions to magnetic-susceptibility tensors, is not an experimentally accessible quantity — see ref. 162 and Chapter VIII). Alternatively (or in addition) relative "ring-current" intensities have been reported [see refs. 131, 132, 114, 120, 116, 156, 19, 82, 111, 140 and 141]. The London-McWeeny method based on various iteratively self-consistent HMO-wave-functions has also been used to calculate "ring-current" intensities^{30,163,164}, magnetic anisotropies^{159,165,32,33,166} and proton chemical-shifts^{165b}. Finally, over the years, several authors have been concerned with investigating the severity of the approximation involved in neglecting overlap integrals between adjacent atoms of the conjugated system; particularly thorough studies have been made by Brooks¹⁶⁷, Wheland and Matlow¹⁶⁸, and Caralp and Hoarau¹⁶⁹; Mayot et al.^{150b} have examined this in the case of phthalocyanins. The general conclusion seems to be that if the results are expressed as a ratio to the corresponding quantities for benzene little significant improvement is achieved when this particular refinement is implemented.

FIGURE 1.4

Experiment-vs.-Theory Regression-Line (Equation (1.98))

With (B'_r/B'_{benzene})-Ratios Calculated via the McWeeny Method



As for other ^1H -NMR applications of the London-McWeeny method, equation (1.94) has been used by Memory *et al.*,^{170,171} Roberts,¹⁷² and by the present author and Haigh and Armour^{140,141,173} to calculate "ring-current" secondary magnetic-fields in a large number of conjugated hydrocarbons. The common practice is to calculate the quantity B'_r/B'_{benzene} (often referred to as the 'sigma ratio' of the proton in question); B'_r is the secondary magnetic-field at the r^{th} proton, brought about by the π -electron "ring-currents" in all rings of the molecule, and B'_{benzene} is the similarly calculated secondary-field at the position of a standard benzene-proton, due to the (unit) "ring-current" in benzene. By using accurate experimental chemical-shift data obtained for this purpose under consistent conditions of solvent and concentration^{60,174}, Haigh *et al.*¹⁴⁰ were able to obtain a very satisfactory regression-correlation between sigma ratios calculated on the McWeeny theory and experimental chemical-shifts, $\{\tau_r^{\text{obs}}\}$, in a sample of 66 sterically unhindered protons in 16 different, planar, condensed, benzenoid hydrocarbons comprising between one and seven rings. The regression line (correlation coefficient: 0.96) is

$$\tau_r^{\text{obs}} = -1.56 (B'_r/B'_{\text{benzene}}) + 4.34 \quad (1.98)$$

This line is reproduced in Figure 1.4. The ^1H -NMR data used for this regression^{60,174} were all measured from full, second-order, iterative analyses of high-field (up to 220 MHz) spectra taken at (or near) 'infinite dilution' in a single solvent (CCl_4) chosen for its reasonably isotropic nature*. This set of chemical shifts seems now to have become a standard one with which the quantitative predictions of subsequent theories of the

* The importance of concentration- and solvent effects on ^1H -NMR shifts in conjugated hydrocarbons has been stressed elsewhere.^{60,174,38a,111,63}

"ring-current" effect have been compared.¹⁷⁵⁻¹⁷⁹ This has certainly been the case for several of the SCF "ring-current" theories discussed in the next sub-section¹⁷⁵⁻¹⁷⁹; these proton-chemical-shift data will also be used in Chapters II, III and IV of the present Thesis, when the predictions of several different theories of such shifts are confronted with experiment.

The McWeeny theory, based on an HMO-formalism, has been applied to heterocycles by Veillard¹⁸⁰ and by Ege and Vogler¹⁸¹ and (based on a modified wave-function) by Vincent et al.¹⁸² Using an HMO which is self-consistent with respect to resonance integrals, Figeys¹⁶³ observed slight changes in the "ring-current" intensities calculated for several condensed, benzenoid hydrocarbons; he then proceeded to use a modified Johnson-Bovey method¹¹⁷ to estimate "ring-current" ¹H-NMR chemical-shifts in these molecules, with some success.¹⁶³ Finally, Parker and Memory¹⁸³ have questioned (and relaxed) several of the assumptions made in the perturbation expansion of the McWeeny method, but have found that, when applied to naphthalene, their modifications did not significantly change the theoretical predictions, provided that the results were expressed as a ratio to the corresponding quantities calculated, by the same method, for benzene.^{183,111}

As for 'out-of-plane' applications of the London-McWeeny method (discussed in the previous sub-sub-section), Ege and Vogler¹⁸⁴ have calculated the magnetic susceptibilities and ¹H-NMR chemical-shifts in macrocyclic corannulenes and 'circumacenes'. Many organic- and biochemical authors (for recent examples see refs. 185-188) are now seeking to obtain a 'second opinion' on the predictions of the Johnson-Bovey^{117,118} tables (mentioned in §1.3 (v) (b)) by also using the Haigh-Mallion¹³⁸ tables referred to in §1.4 (i) (j). The present author²⁸ feels, however, that

there is, unfortunately, a little too much 'blind faith' displayed in the general use of tables of this sort. Neither set of tables is a panacea for the problem they both try to solve; the Johnson-Bovey tables overestimate¹²² the "ring-current" deshielding in the 'deshielding zone' in and near the plane of a benzenoid ring, while there is now abundant evidence to show that the Haigh-Mallion tables, although quite good in the deshielding region¹⁴⁰, underestimate shielding in the 'shielding cone' above the plane of a benzene ring^{38b,185,186} (the latter because of particularly serious breakdown, in that region of space, of the London integral-approximations (§1.4(i)(e)) — see ref. 38b).*

(ii) Formalisms based on Self-Consistent-Field π -Electron Wave-Functions

(a) General Introduction

After a couple of early, isolated contributions from two Japanese groups^{190,191} (which, in a sense, were considerably ahead of their time since they predated the widespread use of computers) the era of self-consistent-field (SCF) extensions to the Hückel-London-McWeeny method really got underway in 1962 with the now-classic paper of Hall and Hardisson.¹⁹² In spite of other developments which have been proposed in the intervening years (which will be reviewed in this sub-section) the latter probably represents the most satisfactory semi-empirical formalism yet available for π -electron systems — at least until recent efforts to avoid the London integral-approximation in the calculation of magnetic

* In a recent review²⁸, the present author has ventured to suggest that, until such time as a set of quantum-mechanical tables is available which makes no appeal to the London integral-approximation, perhaps judicious exploitation of the (fortuitous) complementary nature of the two tables, referred to in the text above, should be advised. Certain (but somewhat ad hominem) attempts have been made by Roberts^{177,189} to circumvent the London approximation, at least partially, in calculations (specifically) on condensed, benzenoid hydrocarbons. After this chapter was written, the author expanded these ideas further in an invited lecture given at the 11th Jerusalem Symposium on Quantum Chemistry and Biochemistry (published as ref. 304).

susceptibilities^{162,193} and ¹H-NMR chemical-shifts.^{177,189,193} Because, in this Thesis, we are dealing with the simpler theories of the "ring-current" effect (and will not be using any of the SCF-approaches until non-alternant hydrocarbons are encountered in Chapter VIII) we shall review SCF-approaches here much more cursorily than we did the Hückel-London-McWeeny formalism, described in detail in the last sub-section.

The SCF-methods may (somewhat arbitrarily) be divided into two types:

- 1) Those which are essentially SCF-versions of the London-McWeeny method (which, if ¹H-NMR chemical-shifts are to be calculated, involve use of the 'test dipole' described in §1.4(i)(i)) ;
- 2) Those which make appeal to the current-density operator.

(b) SCF Versions of the London-McWeeny Method

In these SCF-approaches it is supposed that the π -electron part of the wave function for a conjugated molecule can be written in the form of a single Slater-determinant as

$$\Psi = [(2n)!]^{-\frac{1}{2}} |\phi_1^{(\alpha)} \phi_1^{(\beta)} \dots \phi_n^{(\alpha)} \phi_n^{(\beta)}| \quad (1.99)$$

and that each molecular orbital, $\phi_i^{(\alpha)}$, satisfies the Hartree-Fock equation

$$\left[\frac{p^2}{2m} + V \right] \phi_i^{(\alpha)} = \epsilon_i \phi_i^{(\alpha)}, \quad (1.100)$$

where V includes nuclear-potential terms, σ -core terms and Coulomb- and exchange potentials. The usual LCAO-approximation is invoked that each $\phi_i^{(\alpha)}$ can be expressed as a linear combination of $2p_z$ -like orthonormal atomic-orbitals, one centred on each atom of the conjugation network: i.e.,

$$\phi_i^{(\alpha)} = \sum_s c_{is}^{(\alpha)} \omega_s \quad (1.101)$$

In the presence of the external magnetic-field, B_0 , the momentum operator, $\underline{p}$, goes to $(\underline{p} + e\mathbf{A})$, where $\mathbf{A}$ is given by equation (1.33) or, if the test dipole (§1.4(i) (i)) is also present, by equation (1.83).

At this point, a complication enters the SCF theory, arising from the fact that the potential, V , in (1.100) is a function of the molecular orbitals. Consequently, when $\underline{p} \rightarrow \underline{p} + e\mathbf{A}$ in (1.100), the orbitals are changed; there will thus be a change in V and hence a further change in the orbitals, and so on. In the language of perturbation theory, the method of calculation which takes this dependence on V into account is called the coupled Hartree-Fock procedure. This is the approach adopted by Hall and Hardisson¹⁹³.

Amos and Roberts¹⁹⁴, however, have suggested another method, which has become known as the uncoupled Hartree-Fock procedure, in which this dependence of V on the orbitals is not taken into account, so that V is a function of the unperturbed orbitals, $\{\phi_i^{(0)}\}$, only. Amos and Roberts¹⁹⁴ are of the opinion that this leads to a considerable simplification, both from a theoretical and a practical point of view (though the latter has been disputed in the Literature^{176b,83}, and the present author, for one, is not convinced about the former!). Amos and Roberts¹⁹⁴ have also claimed that when 'suitable' correcting-terms are included (this being the so-called Feenberg-Goldhammer 'geometric'-correction¹⁹⁵⁻¹⁹⁷) the uncoupled method gives a final result which should differ little from that of the "more-complicated"¹⁹⁴ coupled procedure. Roberts has very recently¹⁹⁸ given an upper bound for the error involved in applying this 'geometric' approximation (by means of which a 'coupled' Hartree-Fock calculation is simulated from an 'uncoupled' one.) This error was found* to vary from some 2% in the case of 11,12 benzofluoran-

* A reservation must, unfortunately, be made about these figures. Dr. A.J. Sadzej¹⁹⁹ (Polish Academy of Sciences, Warsaw) has informed the present writer that he has found an error in the Appendix to the paper by Burrows,²⁰⁰ on which Roberts' paper¹⁹⁸, presently under discussion, was based.

there, to zero in the case of benzene (where the first-order corrections to the bond-order matrix — due to the presence of the external magnetic-field — are identically zero when the origin is chosen at the ring centre, thereby making the coupled and uncoupled procedures exactly equivalent when applied to this molecule).

In this uncoupled procedure, the equations to be solved in the presence of the field are then¹⁹⁴

$$\left\{ \frac{1}{2m} [\underline{p} + e\underline{A}]^2 + V \right\} \phi_i = \epsilon_i \phi_i \quad (1.102)$$

where the $\{\phi_i\}$ are the new molecular-orbitals and V is the potential for the unperturbed system. As in the original London-method (§1.4 (i)), ϕ_i is expressed as a linear combination of GIAO's, $\{\chi_s\}$, where

$$\chi_s(r) = \omega_s \exp\left(-\frac{ieB_0}{2\hbar} \underline{k} \times \underline{R}_s \cdot \underline{r}\right). \quad (1.103)$$

The GIAO's are thus obtained by multiplying the usual 'field-free' AO's, ω_s , (usually p_z Slater-functions), by a complex exponential-factor :

$$\omega_s = \frac{1}{\sqrt{\pi}} \zeta^{5/2} \exp(-\zeta r_s). \quad (1.104)$$

In (1.103) and (1.104), $\underline{R}_s$ is again the vector relating the centre of orbital χ_s to the origin of coordinates, and $\underline{r}_s = |\underline{r} - \underline{R}_s|$. ζ is the orbital exponent¹⁶²

The new orbitals will then be

$$\phi_i = \sum_s c_{is} \chi_s \quad (1.105)$$

and the coefficients, $\{c_{is}\}$, can be obtained as eigenvectors of the Hamiltonian matrix, provided it is assumed that the GIAO's are orthogonal. This is the basis set used initially in both the coupled¹⁹² and uncoupled¹⁹⁴ Hartree-Fock formalisms based on a Pariser-Parr-Pople (PPP) π -electron wave-

function^{201,202}. Caralp and Hoarau, on the other hand,²⁰³ have used basis functions in which an AO corrected up to second order in B_0 (for a vector potential with gauge origin at the centre of the atom in question) is multiplied by the same exponential-factor as above:

$$\chi_s(\underline{r}) = N(B_0) \omega_s(\underline{r}) [1 + g(\underline{r}_s) B_0^2] \exp \left\{ -\frac{ie}{\hbar} B \underline{k} \times \underline{R}_s \cdot \underline{r} \right\} \quad (1.105)$$

where N is a normalisation constant and $g(\underline{r}_s)$ is a function proportional to $(x_s^2 + y_s^2)$. These orbitals — which might be termed 'gauge-invariant field-modified AO's' — differ from the usual GIAO's (equation (1.103)) only by this term second-order in B_0 . Most authors (e.g. see ref. 162) have chosen (1.103).

Since the method will be used in Chapter VIII we quote here the coupled Hartree-Fock equations arising from the approach of Hall and Hardisson^{192,176b}. The contributions of "ring currents" to shielding constants and magnetic susceptibility are given by equations (1.107) and (1.108), respectively, where $\mathbb{H}$ is the core-Hamiltonian matrix and $\mathbb{P}'$, defined by equation (1.109), is the the first-order correction (due to the presence of the external magnetic-field, B_0) to the charge-bond-order matrix, $\mathbb{P}$.

$$B' \propto \left(\frac{1}{3} \right) \left(\frac{\mu_0}{4\pi} \right) \left[\left(\frac{e}{\hbar} \right)^2 \sum_{\ell m} s_{\ell m}^2 k_{\ell m} H_{\ell m} P_{\ell m} + \left(\frac{e}{\hbar} \right) s_{\ell m} k_{\ell m} H_{\ell m} P'_{\ell m} \right] \quad (1.107)$$

$$\chi_{\perp}^{\pi \text{London}} \propto \left(\frac{e}{\hbar} \right)^2 \sum_{\ell m} s_{\ell m}^2 H_{\ell m} P_{\ell m} + \left(\frac{e}{\hbar} \right) \sum_{\ell m} s_{\ell m} H_{\ell m} P'_{\ell m} \quad (1.108)$$

with

$$P'_{\ell m} = 2 \sum_i^{\text{occ}} (c'_{\ell i} c_{mi}^{(o)} - c_{\ell i}^{(o)} c'_{mi}) \quad (1.109)$$

and in which $s_{\ell m}$ and $k_{\ell m}$ have the same significance as they had in §1.4 (i)(i) (in the vicinity of equation (1.90)), and the primes indicate orders of expansion in terms of the external field, B_0 . The first-order corrections, c' , to the unperturbed eigenvectors, c , are found by solving

the perturbation problem (1.110) where F' is the first-order correction to the Fock-matrix, F .

$$(F - \mathbb{I} \epsilon) c' = F' c \quad (1.110)$$

$$F_{\ell m} = \left(\frac{e}{h} \right) s_{\ell m} H_{\ell m} - \frac{1}{2} P'_{\ell m} \gamma_{\ell m} \quad (1.111)$$

Since F' is defined via P' , equation (1.110) must be solved by use of an iterative procedure in order to obtain self-consistent matrices.

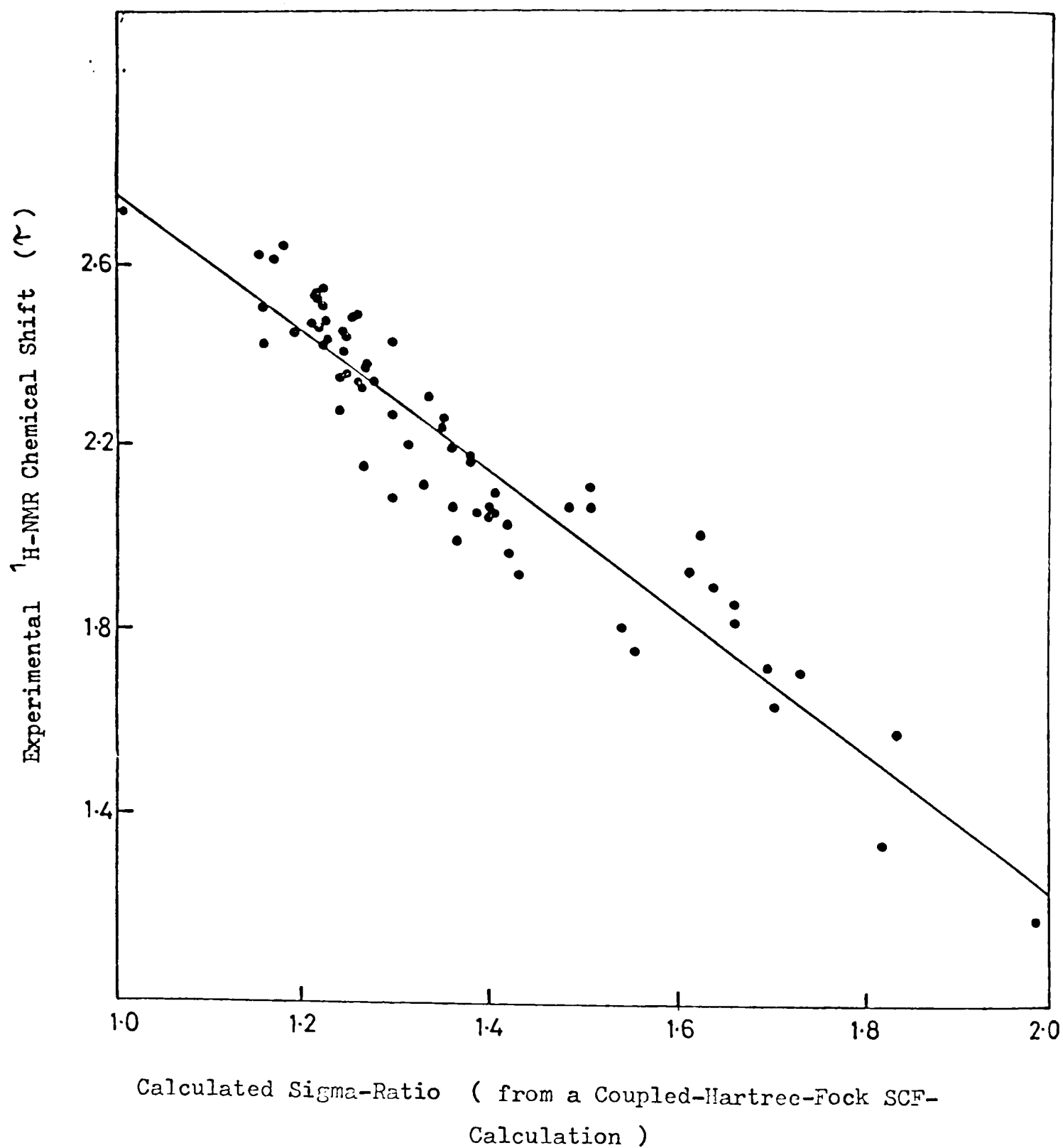
Hall and Hardisson applied this formalism to hydrocarbons^{192a}, and to heterocycles²⁰⁴. They concluded that the use of SCF wave-functions was a considerable improvement in the case of heterocycles, but made no significant change in the predicted chemical-shifts when applied to hydrocarbons. Black et al.²⁰⁵ have also made an extensive study of heterocyclic, conjugated systems via an adaptation* of the Hall-Hardisson method which they call their 'Variable-Electronegativity SCF' approach*. The Hall-Hardisson method has also been applied by Giessner-Prettre and Pullman to calculate magnetic anisotropies,^{206a} "ring-current" intensities and ¹H-NMR chemical-shifts^{206b,c} in pyrimidine and other molecules of biological interest, while Mikami et al.²⁰⁷, and Ege and Vogler¹⁷⁹ have recently applied it (the latter with iteratively variable resonance - integrals and the former with similarly-varied resonance- and two-centre repulsion-integrals) to calculate nuclear shielding¹⁷⁹ and/or magnetic anisotropies^{207,179} of non-benzenoid hydrocarbons, many of which display paramagnetic π -electron-properties. (This will be a subject for discussion in Chapter VIII of the present Thesis).

The most systematic appraisal of the coupled-Hartree-Fock PPP Hall-Hardisson approach is that published by Lazzeretti and Taddei^{176b}. Using

* Note that Black et al., in ref. 205, point out a correction to equations (5.30) and (5.32) of Hall and Hardisson's original paper (ref. 192).

FIGURE 1.5

Experiment-vs.-Theory Regression-Line (Equation (1.112)) with
 (B'_r/B'_{benzene}) ('Sigma'-) Ratios Calculated via the Hall-Hardisson
 Coupled-Hatree-Fock SCF-Method



almost the same experimental data^{60,174} as Haigh et al.¹⁴⁰ had used to obtain equation (1.98) from the Hückel-McWeeny formalism, they obtained the following correlation-line (Bravais index:0.94) between $\{\tau_r^{\text{exp}}\}$ and 'sigma ratios' calculated by Hall and Hardisson's method:

$$\tau_r^{\text{exp}} = - 1.52 (B'_r/B'_{\text{benzene}}) + 4.28 \quad (1.112)$$

This correlation line is illustrated in Figure 1.5; this implies that the "ring-current" contribution to the chemical shift of a benzene proton is ca. 1.52 ppm — to be compared with 1.56 ppm obtained from equation (1.98) via the Hückel-McWeeny method and an early 'experimental' estimate²⁰⁸ of 1.55 ppm. It is instructive to compare this also with the value of 1.20 ppm obtained by Vysotskii²⁰⁹ who, by use of coupled Hartree-Fock perturbation-theory, has derived expressions for both 'local' and 'non-local'. (i.e. "ring-current") contributions to the ^1H -shielding in benzene. (An interesting feature of the 'non-local' contribution is that, with certain limiting simplifications, the expression for it transforms to the classical formula of Waugh and Fessenden¹⁵ for two current loops). The difference between the values of ca. 1.5 ppm obtained from equations (1.98) and (1.112) and that of 1.20 ppm reported by Vysotskii²⁰⁹ may²¹⁰ reflect the contribution of local bond-anisotropies (see also §1.7) — Vysotskii does not give the calculated 'local'-contribution for benzene.

The uncoupled Hartree-Fock version of the Hall-Hardisson method, developed by Amos and Roberts for magnetic susceptibilities¹⁹⁴ and ^1H -NMR chemical-shifts,¹⁷² has been applied to heterocycles^{211,83} and to substituted benzenes²¹², whilst Lazzeretti¹⁷⁸ has developed the Hartree-Fock perturbative approach in terms of the uncoupled first-order density-matrix. Uncoupled Hartree-Fock calculations on the magnetic properties of conjugated systems have recently been the subject of some controversy²⁸ since the relative order of magnetic anisotropy of benzene, pyrrole, furan and thiophen

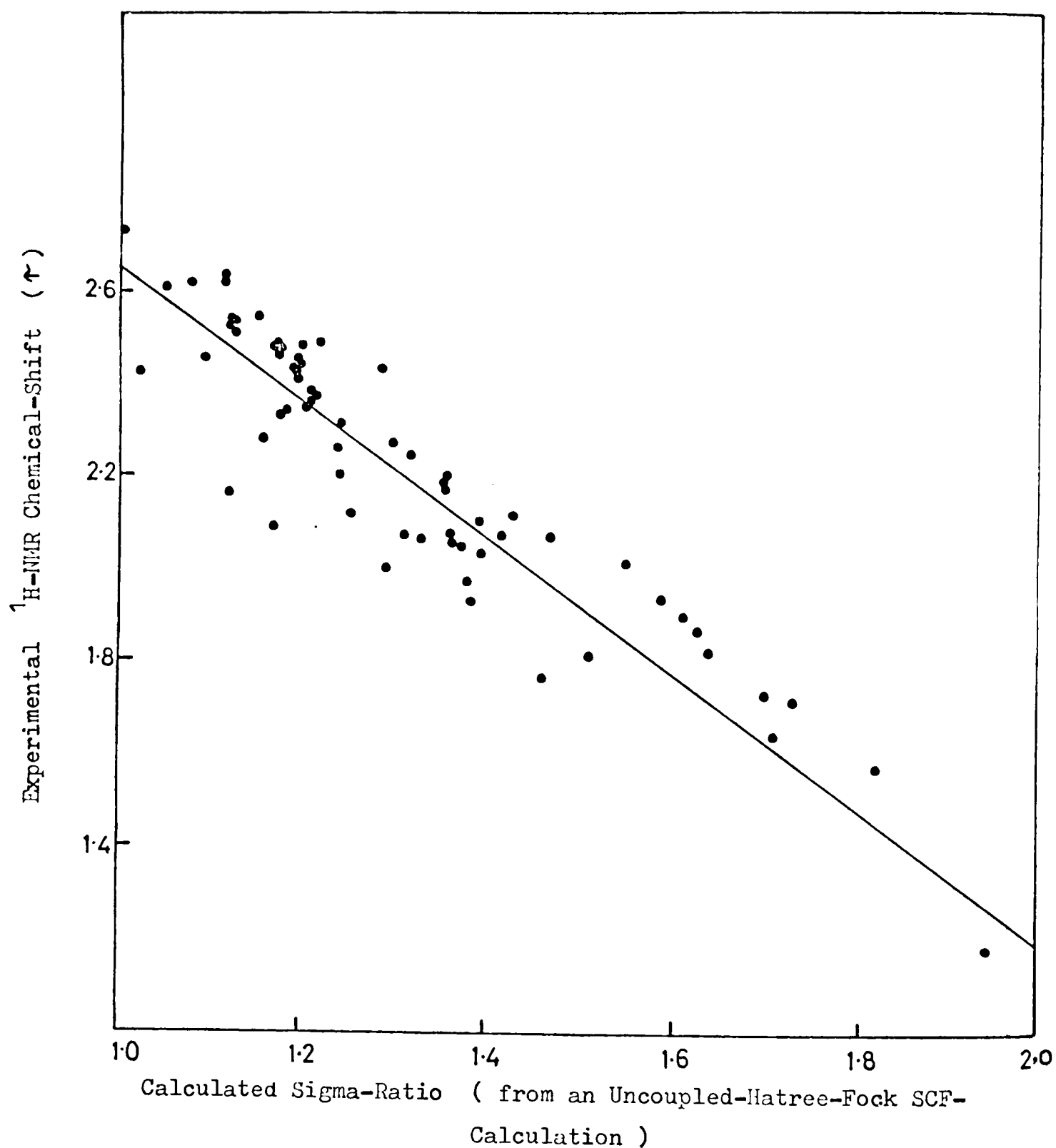
calculated by Corradi *et al.*⁸³ using the Amos-Roberts method¹⁹⁴ is different from that obtained previously by Davies²¹³ using what is essentially an 'uncoupled' method without the 'geometric'^{196,197} correction.²¹⁴ This discrepancy is, perhaps, not surprising since the two investigations used different methods of calculation and different parametrisations; nevertheless, the remarks of Corradi *et al.*⁸³ have provoked critical comment from Davies²¹⁵ and, in turn, a reply from Lazzeretti and Taddei.²¹⁶ The controversy seems to be centred mainly around the question of parametrisations, though, on a more fundamental level, it should not be overlooked that the two methods of calculation employed are different; in particular, in Davies' 'finite-perturbation' method²¹⁴, the charge-bond-order matrix, $\mathbb{P}$, is regarded as being unchanged in the presence of a magnetic field, whereas in the coupled Hartree-Fock method of Hall and Hardisson¹⁹² (and also in the uncoupled versions of it^{172,194}, when the 'geometric' correction^{195,197} is applied) this is, in general, not so. Both the present author²⁸, and Roberts²¹⁷, have commented independently to this effect.

The uncoupled Hartree-Fock theory of Roberts¹⁷² has been applied to calculate the ^1H -NMR shielding-constants in a large number of condensed, benzenoid hydrocarbons by Lazzeretti and Taddei^{176a} and (apparently independently, though two years later) by Long and Memory²¹⁸. The latter workers merely concluded qualitatively that SCF-values show no improvement over the HMO - predicted chemical-shifts of Haigh *et al.*¹⁴⁰ when only ratios (to benzene) are considered but that absolute magnitudes are considerably better. Lazzeretti and Taddei^{176a}, on the other hand, performed a systematic regression-analysis (analogous to that given in equation (1.112) for the coupled procedure) between $\{\tau_r^{\text{exp}}\}$ ^{60,174} and sigma ratios $(B'_r/B'_{\text{benzene}})$ calculated via the Roberts 'uncoupled'-formalism¹⁷², obtaining:

$$\tau_r^{\text{exp}} = -1.46 (B'_r/B'_{\text{benzene}}) + 4.11 \quad (1.113)$$

FIGURE 1.6

Experiment-vs.-Theory Regression-Line (Equation (1.113)) with
 (B_r'/B_{benzene}') ('Sigma'-) Ratios Calculated via the Amos-Roberts
 Uncoupled-Hartree-Fock SCF-Method



(correlation coefficient: 0.91). This is to be compared with equations (1.98) and (1.112). This regression line is illustrated in Figure 1.6; it predicts the "ring-current" contribution to the downfield-shift of a benzene proton to be 1.46 ppm.

It is, however, possible that the calculations discussed in the previous paragraph may have to be disregarded, for the original formalism of Roberts^{172a} contained a mistake, and it is not at all clear that the above calculations were based on the corrected version^{172b} of Roberts' method^{172a}, which the latter author gave in a later paper^{172b}. The error is concerned with equation (1.83); in this equation, the term $\frac{1}{2}B_0 \times \underline{r}$ is independent of the choice of origin for the vector $\underline{r}$ (as was much discussed in §1.4(i)(c)), but the vector $\underline{r}$ which appears in the second term of equation (1.83), $\frac{\mu_0}{4\pi} \frac{\underline{r} \times \underline{k}}{r^3}$, must have its origin at the position of the 'test' dipole of moment $\underline{mk}$. Of course, when the Amos-Roberts formalism was applied only to calculate magnetic susceptibilities¹⁹⁴ this problem did not arise, for the 'test' dipole was not then required and so equation (1.83) became equation (1.33) with only the one, origin-independent term. When the uncoupled approach is used to calculate chemical shifts¹⁷², however, the 'test-dipole' contribution to the vector potential is conventionally included (but see ref. 219 and the discussion in Chapter III and Appendix A) and it was the fixed-origin nature of the vector $\underline{r}$ appearing in this term which was overlooked in Roberts' original treatment^{172a}, and which was corrected for in ref. 172b. It seems likely²²⁰ that the calculations of refs. 176a and 218 were based on the formalism given in ref. 172a rather than that in ref. 172b and, as such, must be regarded with some caution.

The present writer is in any case inclined to feel that this uncertainty about some calculations based on the uncoupled Hartree-Fock SCF-method is no great privation for, in his opinion, the method lacks

both the simple elegance of the HMO-approach and the (relative) rigour* of the coupled Hartree-Fock SCF-formalism. From a practical point of view, its computational advantages over the coupled approach have, in the opinion of some,^{176b,179} been exaggerated, while, from an aesthetic point of view, the 'geometric' approximation (though, numerically, apparently unassailable^{198**}) seems theoretically somewhat unsatisfactory. Then there is also the question of gauge-invariance of calculated magnetic-properties. In principle, coupled Hartree-Fock results are gauge-independent only within the limit of infinite basis-sets²²²⁻²²⁴ whereas, in actual computations, a limited GIAO-basis is used^{137,194,176b,225}. In practice, the Hall-Hardisson coupled-Hartree-Fock procedure, precisely because it is based on a GIAO-scheme^{194,226} (see below), is at least origin-independent^{192,176b,226} while the uncoupled approach is not^{172,194} (though, when the geometric approximation is applied, it is nearly so^{172,194}). From §§1.4 (i)(c) and 1.4 (i)(f) it is also clear that the simple Hückel-McWeeny formalism is rigorously origin-independent. The uncoupled procedure is therefore found wanting on the three criteria of elegance, practicality and origin-independence, and it is for these reasons that the present author would always prefer to perform a simple Hückel-London-McWeeny calculation or a full, coupled-Hartree-Fock Hall-Hardisson SCF-one. Accordingly, this is the policy which will be adopted in the present Thesis.

Whilst once again on the subject of gauge-invariance, we consider some recent comments of Sadlej²²⁷ on the use of so-called Gauge-Invariant Atomic-Orbitals (equations (1.29) and (1.30)). As Sadlej emphasises²²⁷, these orbitals simply represent a very specific choice of the basis set in

* It may, on the face of it, appear absurd to talk of 'rigour' in the context of a method which is still, after all, based on a single-determinantal π -electron wave-function; however, in the present state of this field, although a formalism for Gauge-Invariant (Gaussian) Atomic-Orbitals in an ab-initio scheme is available^{221,229} applying it to calculate the magnetic properties of large, polycyclic, conjugated systems of the type considered in this Thesis is, as yet, probably not practicable.

** But see the footnote on page 64.

a calculation of magnetic properties. As we have seen (§1.4(i)(c)), the basis sets for different gauge-origins are connected by a unitary transformation¹³⁷ and this assures a complete gauge-origin independence of the computed energies²²⁸. In a GIAO-scheme this feature does not, however, depend on the degree of completeness of the basis set; hence, within the GIAO-approach, even what are, by many people's criteria, very poor calculations (such as, for example, the simple Hückel one) will be gauge-origin independent. A GIAO-formalism does not, therefore, offer any possibility of an a priori assessment of the inaccuracy of such results²²⁷. Moreover, Sadlej has emphasised²²⁷ that the use of a coupled-Hartree-Fock scheme with a GIAO-basis-set (such as, for example, in the Hall-Hardisson approach¹⁹²) violates the fundamental Variation-Principle leading to the coupled-Hartree-Fock equations^{229,230} and this is the result of an artificial extension of the basis set for the perturbed orbitals^{227,231*}. Sadlej even goes so far as to state, in ref. 227, that "... in general, there is no physical justification of the computational trick which leads to a complete gauge-invariance of molecular magnetic-properties²³²." There is, of course, much truth in this remark; we shall nevertheless continue to capitalise to a large extent on this 'trick' in the work described in the present Thesis. What we wish to emphasise here, however, is that even using the device of GIAO's within the context of uncoupled Hartree-Fock-theory¹⁹⁴ (even when the Feenberg-Goldhammer¹⁹⁴⁻¹⁹⁷ 'geometric'-correction is applied) is not sufficient to guarantee rigorous origin-independence of the results^{194,199}. This is why, in this Thesis, we have eschewed entirely methods based on uncoupled-Hartree-Fock GIAO wave-functions.

Finally, as a post-script on gauge-invariance, we note the exciting (but perhaps somewhat startling²⁸) recent claim of Weisenthal and de Graaf²³³

* Note the corrections to the numerical data in Tables 7 and 8 of ref. 231 detailed by the present author in Tables 8 and 9 (page 22) of ref. 28.

that by writing the Hamiltonian explicitly in terms of field strengths, $\underline{B}_0$, rather than vector potentials, $\underline{A}$, any question regarding gauge-invariance or best choice of gauge would be obviated. This scheme has been commented on by Moss and Perry²³⁴. Woolley and Cordle have, however, pointed out²³⁵ that such gauge-difficulties are not avoided by making a unitary transformation to a formalism which is independent of the electromagnetic-field potentials, and that neither of the formalisms of Weisenthal and de Graaf²³² possesses the uniqueness that has been attributed to them. By a somewhat different reasoning, Gomes²³⁶ has also independently shown that (unfortunately!) the new Hamiltonian of Weisenthal and de Graaf²³³, which is apparently and superficially gauge-invariant, does, in fact, implicitly involve a particular choice of gauge for the vector potential, and that it has, therefore, none of the advantages which have been claimed for it²³⁶.

(c) Approaches which make Appeal to the Current-Density Operator

The commutator identity

$$\underline{v} \equiv [\frac{1}{2}v^2, \underline{r}] \quad (1.114)$$

allows the calculation of magnetic properties to be formulated in one of two basic ways^{81b,175a}. Either the terms involving the differential operator $\underline{v}$ are evaluated as they stand, or equation (1.114) is used and $\frac{1}{2}v^2$ is replaced by a term of the form of a standard Hamiltonian. These sorts of calculation have been classified as of the 'velocity' or 'length' type^{175a}. By 'velocity' type is meant that the formulae for susceptibility and chemical shift — which, when derived, involve the $\underline{v}$ operator — are left in that form whereas by 'length' type is meant that the commutator relation (1.114) has been used to replace terms involving $\underline{v}$ by those involving $\underline{r}$ ^{175a}; the latter transformation was, in fact, used implicitly by London³. All the quantum-mechanical theories of the "ring-current" effect in ¹H-NMR spectroscopy detailed so far have involved introducing a test dipole at the position of the given nucleus in order to probe the secondary field there. This has invariably been done without making specific reference to the current-density operator. The test-dipole formalism is usually (and, in this Thesis, has been) expressed in terms of 'length'. In an important series of papers, Amos and Roberts^{175a} have outlined a more-direct

method of finding this secondary field (and hence of obtaining $^1\text{H-NMR}$ chemical-shifts) via an intermediate calculation of the current density induced in the molecule as a whole (by the vector potential created by the external, applied magnetic-field only), by direct appeal to the current-density operator. This formalism is, therefore, expressed in terms of 'velocity',^{175a}.

The current density associated with the j^{th} electron (of, for example, an $N - \pi$ -electron system) at which the external magnetic-field creates a vector potential $\underline{A}_j$, and the wave function of which is ψ , is given by¹³⁶

$$\underline{J}_j^\pi(\underline{r}_j) = \int \left\{ \frac{\hbar e}{2mi} (\psi \nabla_j \psi^* - \psi^* \nabla_j \psi) - \frac{e^2}{m} \underline{A}_j \psi^* \psi \right\} d\tau_1 d\tau_2 \dots d\tau_{j-1} ds_j d\tau_{j+1} \dots d\tau_N, \quad (1.115)$$

where $d\tau$ indicates integration over space and spin and ds over spin only.

The total current-density is found by summing over the $\underline{J}_j^\pi(\underline{r}_j)$ which, because of the Pauli Principle, are all identical^{175a}. Hence:

$$\underline{J}^\pi(\underline{r}) = N \underline{J}_j^\pi(\underline{r}_j) \quad (1.116).$$

In principle (and, indeed, in practice^{175a}), $\underline{J}^\pi(\underline{r})$ can be computed from approximate, GIAO-SCF π -electron wave-functions of the type described in §1.4(ii)(b). The secondary field, $\underline{B}'$, at any point $\underline{r}$ due to this current-density is then obtained via a classical Biot-Savart formalism:

$$\underline{B}' = -\frac{\mu_0}{4\pi} \frac{1}{3} \int \frac{\underline{r} \times \underline{J}^\pi(\underline{r})}{r^3} d\underline{r} \quad (1.117)$$

Amos and Roberts^{175a} have further demonstrated that, when based on the coupled-Hartree-Fock method, these computed current-densities, $\underline{J}^\pi(\underline{r})$, are gauge-invariant. These authors also showed that, within the context of a GIAO-SCF π -electron wave-function, the most-important contributions to computed current-densities come (not surprisingly, perhaps) from bonded centres within the conjugation network; so much so that, by a judicious

neglect of certain non-bonded terms, Amos and Roberts were able to retrieve the concept of a "bond current-density". When calculated by means of an uncoupled method with Feenberg-Goldhammer correction¹⁹⁴⁻¹⁹⁷, these bond current-densities exhibited a non-conservation to the extent of ca. 6% around the perimeter of naphthalene^{175a}.

Using various versions of the London integral-approximation (see §1.4 (iii)) Amos and Roberts^{175a} have applied their current-density formalism to calculate ^1H NMR-shifts in benzene and naphthalene, and have further shown, somewhat surprisingly*, that the current-density and test-dipole formalisms lead to the same expressions for ^1H -NMR chemical-shifts^{175c}. Edwards and McWeeny¹⁹³ have used a density-matrix formulation of the coupled-Hartree-Fock perturbation-theory^{237,238} to calculate magnetic susceptibilities and ^1H -NMR chemical-shifts directly from the current-density expression. Their calculations have taken into account some very salient comments (made earlier by McWeeny)²¹⁹ about gauge invariance, the repercussions of which on the simple London-McWeeny theory¹³² will be examined in detail in Chapter III of this Thesis. Essentially, McWeeny points out²¹⁹ that a distinction must be made between 'gauge invariance' in the sense of origin independence of calculated results as the origin of coordinates is arbitrarily varied, and invariance of the calculated properties to translation of the molecule through the uniform field (B_0). Furthermore, McWeeny has disputed²¹⁹ the necessity — and, indeed, questioned the propriety — of including a dipole contribution in the vector potential appearing in the exponential gauge-factor in

* In view of the analysis presented in Appendix A of the present Thesis, it is surprising the Amos and Roberts should find that the current-density and test-dipole formalisms lead to the same results when they are both based on an approximate wave-function. Close examination of refs. 175c and 175a shows that this conclusion may have been predestined by the neglect, in equation (21) of ref. 175c, of a vector-potential contribution from the test dipole¹⁹⁹.

equations (1. 29) and (1. 30) when nuclear shieldings are to be calculated (a device which McWeeny himself had earlier suggested);¹³² all that should be evaluated by first-order perturbation theory, according to McWeeny²¹⁹, is the coupling energy between the 'test' dipole and the required secondary-field using, as the unperturbed wave-function, the exact uniform-field solution in the absence of the dipole²¹⁹. This is precisely what is done in the GIAO current-density approaches dealt with in this sub-sub-section, but not in the 'test-dipole' approaches described in 1.4 (ii)(b). This question is taken up further, in the context of semi-empirical "ring-current" theories, in Chapter III and, on the basis of exact calculations, in Appendix A.

Finally, by picking out those terms in the current density which are first order in B_0 , Coulson, Gomes and the present author¹⁶² have used the current-density formalism to derive, within the context of SCF- π -electron theory, an exact expression for χ^π which makes minimal appeal to the London integral-approximation (see next sub-sub-section (§ 1.4(ii)(d))).

(iii) Avoidance of the London Integral-Approximation

As was explained in detail in § 1.4 (i)(e), the London integral-approximation consisted essentially in replacing $\underline{r}$ (equation (1. 30)), a vector relating the position of an electron in a given orbital to an arbitrary origin, by the quantity $\frac{1}{2}(\underline{R}_s + \underline{R}_t)$ in the vicinity of the bond s-t of the conjugated system; $\underline{R}_s$ and $\underline{R}_t$ are the vectors relating the atoms s and t, respectively, of the conjugated system, to this same origin. This procedure vastly simplifies many of the integrals which arise in the magnetic theory (§1.4(i)(e)).

Calculations which make attempts to avoid this approximation divide themselves into three types: (1) certain calculations on benzene in which the approximation has been obviated completely^{203,162}; (2) those in which all integrals are evaluated numerically, but in which the London approximation is still implicitly invoked in the calculation of $\mathcal{P}'$

(the first-order correction to the bond-order matrix in the presence of the external magnetic-field) via the coupled-(or uncoupled-) Hartree-Fock procedure¹⁶²; (3) those calculations which use the same procedure as (2) for handling P' but in which some integrals are evaluated exactly (by numerical methods) while others are estimated by appeal to various forms of the London integral-approximation^{189,177}.

(1) Careful examination of ref. 192 reveals that, in devising their coupled-Hartree-Fock method for calculating P' , Hall and Hardisson invoked a series of assumptions which (although they are not explicitly labelled as such) are tantamount to making the London approximation. Furthermore, it is by no means an easy matter to calculate P' without following this procedure¹⁶². The same comments apply when P' is calculated via an uncoupled method plus Feenberg-Goldhammer correction¹⁹⁵⁻¹⁹⁷. In the case of a calculation on benzene, however, P' is unchanged in the presence of an external field provided that the origin is taken at the ring centre.^{28,175b} Consequently, in this very special case, if all integrals are evaluated numerically, the London integral-approximation may be avoided completely. Such a procedure has been adopted by Amos and Roberts^{175b}, and by Coulson, Gomes and Mallion¹⁶². On application of various different forms of the London approximation (see below), Amos and Roberts^{175b} found that the π -electron susceptibility of benzene varied over a range of ca. 25%. The value taken for the orbital exponent, ζ (equation (1.104)), was also an important factor. Coulson et al.¹⁶² have reported agreement with Amos and Roberts^{175b} on the numerical value obtained without use of the London approximation.

(2) If the approximation is used to calculate P' via the Hall-Hardisson method, but is otherwise avoided by numerical evaluation of all other integrals, calculations on arbitrary, polycyclic, conjugated hydrocarbons may successfully be carried out, as Coulson, Gomes and the

present author¹⁶² have recently demonstrated. Caralp and Hoarau²⁰³ performed a special perturbation-calculation (also based on a Goeppert-Mayer and Sklar formalism²³⁹), with gauge-invariant field-modified atomic-orbitals determined up to second order in the field (equation (1.106)). Their numerical results on a number of alternant hydrocarbons agreed with those calculated by Coulson et al.¹⁶², using the method described in ref. 162, to within 1.5%. Coulson, Gomes and Mallion¹⁶² have commented that this good agreement between the two sets of calculations provides a reassuring check on Caralp and Hoarau's method,²⁰³ and on their own method¹⁶², of calculating χ_1^π ; it also reflects well on Hall and Hardisson's coupled-Hartree-Fock procedure¹⁹² for estimating $\mathbb{P}'$. Coulson et al.¹⁶² are of the opinion that the concordance between the two sets of calculations is probably a more reliable test of the validity of this latter procedure than comparisons of predictions based on it with experimental data on total susceptibilities (which, as has been much discussed — e.g. refs. 162 and 240 — are fraught with difficulties).

The London approximation was, of course, originally formulated in the context of magnetic-susceptibility calculations; when it comes to calculating chemical shifts, however, terms in $1/r^3$ occur, and then there arises the question of whether to use the substitution

$$1/r^3 \rightarrow 1/|\frac{1}{2}(\underline{R}_s + \underline{R}_t)|^3 \quad (1.118)$$

(which Roberts¹⁷⁷ designates 'LAI') or whether the substitution

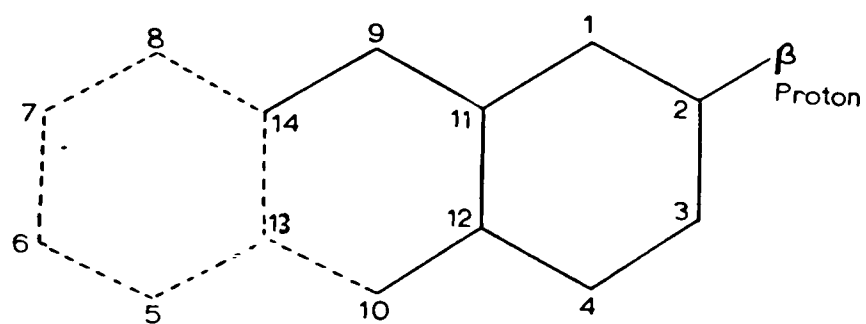
$$1/r^3 \rightarrow \frac{1}{2}(1/R_s^3 + 1/R_t^3) \quad (1.119)$$

(called 'LAII' by Roberts¹⁷⁷) is more appropriate. Amos and Roberts have even suggested a third form^{175b,c} ('LA III'):

$$1/r^3 \rightarrow c(1/R_s^3 + 1/R_t^3). \quad (1.120)$$

FIGURE 1.7

Illustration of Roberts' "Four-Bond
Policy" (Concerning the London Integral-
Approximation) as Applied to Anthracene



(See text opposite - page 79 - for details)

in which c is taken to be 0.2.

As is intuitively reasonable, these approximations all improve considerably as the distance of the bond $s-t$ from the proton in question increases²⁸. Roberts¹⁷⁷ has tabulated numerical data for the β -proton (Martin's terminology²⁴¹) of anthracene (Figure 1.7). These data show that no significant loss of accuracy would result if 'exact' evaluation of the integrals concerned (*i.e.* evaluation without use of any of LA I, II and III) were to be restricted to bonds 'near' the proton. Roberts finds that the following definition of 'nearness' is suitable in practice: let a given proton, P , be bonded to an atom, a , on the (hexagonal) conjugated network, and let a' be the atom nearest to P on this network; then, an integral involving the $s-t$ bond is evaluated exactly only if this bond can be reached from either a or a' by a walk of four bond-lengths (or fewer) along the network. In the diagram of anthracene shown in Figure 1.7, those bonds which satisfy this criterion for the β -proton are drawn as continuous lines; those whose contributions to the shielding of this proton can 'safely' be estimated by use of the London approximation are depicted as broken lines. Roberts concludes¹⁷⁷ that a combination of LAI and what he calls his 'four-bond policy' gives results which compare satisfactorily with experimental ^1H -NMR shifts^{60,174} — although, curiously, over a wide range of benzenoid hydrocarbons, the experiment-theory deviations follow very similar patterns to those encountered when the simple Hückel-McWeeny method¹³² was applied¹⁴⁰ to the same molecules (β -protons' deviating markedly etc.).

The absolute value, from Roberts' work¹⁷⁷, for the "ring-current" contribution to the ^1H -NMR shift of a benzene proton is -0.72 ppm; this is in good agreement with Pople's 1964 'experimental' estimate²⁴² of ca. 0.7 ppm, though different from recent semi-empirical estimates, from refs. 140, 176 a and b (equations (1.98), (1.113) and (1.112), respectively), of -1.56 , -1.46 and -1.52 ppm. It also differs somewhat from Vysotskii's SCF-

theoretical-value²⁰⁹ of -1.20 ppm.

In some work performed in these laboratories partly under the present writer's supervision*, Coulson, Gomes and the present author^{162,236b} have investigated the repercussions of the London integral-approximation. They considered the identity

$$\underline{r} = \frac{1}{2}(\underline{R}_s + \underline{R}_t) + [\underline{r} - \frac{1}{2}(\underline{R}_s + \underline{R}_t)] \quad (1.121)$$

and, on inserting it into their expression¹⁶² for the first-order electronic current-density in the GIAO - LCAO scheme, obtained

$$M_{st} = \frac{1}{2}k \frac{1}{2}(\underline{R}_s + \underline{R}_t) \times \underline{J}_{st} + \mu_{st} \quad (1.122)$$

for the (s-t) element of the magnetic dipole-moment of the polycyclic, conjugated system in question. In equation (1.122), μ_{st} is the moment about the mid-point between centres s and t, given by

$$\mu_{st} = -\frac{e^2 B_0}{2m} \frac{1}{2} P_{st} \left\{ \int \omega_s^* \rho^2 \omega_t d\tau + |\underline{R}_s - \underline{R}_t|^2 \int \omega_s^* \frac{\zeta y^2}{r_t} \omega_t d\tau \right\}, \quad (1.123)$$

where ρ is the cylindrical radius from an axis parallel with the z-axis (which is perpendicular to the molecular plane) through the mid-point of centres s and t. $\underline{J}_{st}$ in equation (1.122) is the integral of that term in the current density which is first order in B_0 and which involves centres s and t¹⁶². The expression for this is¹⁶²

$$|\underline{J}_{st}| = -\frac{e^2 B_0}{2m} (\underline{k} \cdot \underline{R}_s \times \underline{R}_t P_{st} - \frac{2\hbar}{e} P'_{st}) \left(\int \omega_s^* \frac{\partial}{\partial x} \omega_t d\tau \right) \quad (1.124)$$

along x, the axis directed from t to s.

Now equation (1.122) admits of the following interesting interpretation: the London integral-approximation consists essentially in setting $\underline{r}$ equal to $\frac{1}{2}(\underline{R}_s + \underline{R}_t)$ (equation (1.39)) — that is to say, in making the second

* But it is not included in this Thesis. Details of this work will be found in ref. 162 and in the thesis of Mr. J.A.N.F. Gomes, Linacre College (ref. 236b).

term (in square brackets) in the identity (1.121) exactly zero. Now the first term of equation (1.122), involving J_{st} , arises from the first term of identity (1.121) when the latter is substituted into the expression¹⁶² for the first-order current-density, and it may therefore be thought of as corresponding, in some way, to the 'London' contribution to χ_L^π . The second term, μ_{st} , of (1.122) may then be regarded as a 'correction' to the London estimate. Such a partition of the total π -electron effect into a 'London' and a 'non-London' part allows comparison of the J_{st} -terms calculated from equation (1.124) with previously published (relative) values of "bond-current" densities and "ring currents", which represent just the 'London' contribution to the total π -electron effect. For alternant, condensed, benzenoid hydrocarbons, Coulson et al.¹⁶² found that these two quantities agreed to within ca 5%¹⁶².

1.5 Other Theories of the "Ring-Current" Effect

In this sub-section, we very briefly review a few other, rather-more esoteric, approaches to the "ring-current" idea, which are not conveniently classified under any of the headings used in §§1.3 and 1.4.

Firstly, we mention an early (but nevertheless very sophisticated) attempt by Brooks²⁴³, in 1940, to treat diamagnetic anisotropy of conjugated systems from the standpoint of the Heitler-London theory,²⁴⁴ by inclusion of ionic terms in the secular equation, rather than that of the Hückel-London LCAO-MO approach. He concluded that the "correct approximation" lies between the pure Heitler-London-Pauling-Slater²⁴⁴ and MO-approximations, but that the high value of these anisotropies is best accounted for from the MO-viewpoint²⁴³. In this much-neglected paper, when commenting on the Pauling- and London theories, Brooks also made the following somewhat astute observation (which, so far as the present writer is aware, has never been quoted by other authors though it has been restated by several^{214b,81,245}

over 20 years later): "The fact that both theories [i.e. Pauling's¹ and London's³] are in such good agreement with experiment, in spite of the many approximations involved, is evidence that the ratios of the anisotropies reduce to purely geometrical quantities, which have a significance beyond the particular model adopted for specific calculations".* We shall have more to say along these lines in Chapters VI, VII and VIII of the present Thesis.

An approach which has long been used for calculating the magnetic susceptibilities of simple model-systems is the free-electron model^{246,247} much exploited^{248,22}, in particular, by Rebane.^{249,250} The method has been reviewed very recently by Walnut.²⁵¹ It considers a particle on a one-dimensional, circular track on which it is subject to an arbitrary, finite potential-function. In addition, the particle is subjected to a uniform magnetic-field perpendicular to the plane of the track. So far as its interaction with the magnetic field is concerned, the particle is assumed to have the properties of an electron²⁵¹. The vector potential, $A_0(\underline{r})$, created by the external magnetic-field, B_0 , is then as A in equation (1.33) and, if the track is assumed to lie in the x-y plane, $A_0(\underline{r})$ is then of constant magnitude, A_0 , on the track. With this gauge, the correction to the Hamiltonian which is first order in the field is

$$\mathcal{H}_1 = \frac{1}{2} \left(\frac{e}{m} \right) (A_0 p + p A_0) \quad (1.125)$$

where p is the momentum along the track. The procedure for finding the minimising gauge, originated by Tillieu and Guy²⁵² and by Rebane²⁵⁰, has been reviewed by Hegstrom and Lipscomb²⁵³. In this procedure, the gauge function, f , is adjusted so that the expectation value of $\mathcal{H}_2$ (the

* It is interesting from a historical point of view, to record here the fact that Brooks²⁴³ references this statement with the footnote: "I am indebted to Professor F. London for this observation".

second-order correction to the Hamiltonian equal to $(\frac{e^2}{2m})A_o^2$ is a minimum. The quantity to be minimised is ²⁵¹

$$E_d^{(2)} = \frac{e^2}{2m} \int_0^l \rho (A')^2 ds, \tag{1.126}$$

where $\rho = |\psi^{(o)}|^2$ (1.127).

and $\tilde{A}' = \tilde{A}_o + \frac{df}{ds}$

$\psi^{(o)}$ is a (non-degenerate²⁵¹) solution unperturbed by the external magnetic-field and l and s are, respectively, the circumference of the track and the displacement around the track. The function f_i that minimises $E_d^{(2)}$ satisfies²⁵¹

$$\frac{d(\rho(A_o + df_i/ds))}{ds} = 0 \tag{1.128}.$$

The solution, for nodeless ρ , is²⁵¹

$$f_i = \int_0^s (c/\rho(s'))ds' - A_o s, \tag{1.129}$$

where c is a constant adjusted so that f_i is periodic in s with period l . In the Coulomb-gauge, the function

$$f = h\psi^{(1)} / ie\psi^{(o)} \tag{1.130}$$

satisfies (1.128). Walnut has shown²⁵¹ that f can be further broken down into

$$f = f_i + f_h \tag{1.131}$$

where f_i is given by equation (1.129) and f_h is

$$\left. \begin{aligned} f_h &= \int (b/\rho)ds \\ (\chi_h &= \psi^{(o)} f_h/b) \end{aligned} \right\} \tag{1.132}$$

in which b is a constant. After much further analysis (which we do not

reproduce here), Walnut has shown²⁵¹ that the expression for the current is

$$j = -\text{Re} (\psi^* p \psi) \quad (1.133)$$

when the minimising gauge is used and ψ is the exact wave-function.

With this gauge, the first-order current is

$$j^{(1)} = -\text{Re} \left[-i \left(\frac{e}{h} \right) f_h \psi^{(0)} \left(-i \frac{d}{ds} (\psi^{(0)}) \right) + \psi^{(0)} \left(-i \frac{d}{ds} \left(i \frac{e}{h} f_h \psi^{(0)} \right) \right) \right] \quad (1.134).$$

Walnut's approach²⁵¹ has shown that both the magnetic susceptibility and the current for an orbital can be obtained explicitly from the functions $\psi^{(0)}$ and χ_h (equation (1.132)), and he has claimed that deriving these two functions is particularly straightforward when the potential is formed from square barriers or wells.

There is a vast literature on free-electron calculations, somewhat inadequately reviewed here since it is mainly in the Russian language, with which the present writer is unfamiliar. Representative references of Rebane's work are 249 and 250; key references in Western languages are Baer, Kuhn and Regal²² (in German) and Walnut²⁵¹ (in English) on the latter of which the writer has relied heavily in the above discussion.

Finally, in this sub-section, we note that Stiles et al.²⁵⁴⁻²⁵⁶ have found that multipolar expansions provide a general analytical-formalism for mapping magnetic shielding induced by shift reagents at nuclei of substrate molecules²⁵⁶. They point out that classical expressions for the induced "ring-current" in benzene avoid multipole expansions but suffer from being purely diamagnetic; these authors are therefore of the opinion²⁵⁶ that for macrocyclic systems such as porphyrins multipolar expansions offer an attractive alternative to more-established methods (such as those of Waugh and Fessenden¹⁵ and Johnson and Bovey^{117,118}) based on elliptic-integral

expansions of magnetic shielding due to "ring currents" (see §1.3 (v)(b) and Chapter II of the present Thesis). They also believe²⁵⁴ that their model "... systematically considers finite current-distributions within the context of the quantum-theory of magnetism." They also point out, however, that for large diamagnetic-systems the geometry ensures considerable anisotropy and the effective radii of the induced-current circulations cause the multipolar expansion of the shielding to converge more slowly than is the case for paramagnetic metal-ions²⁵⁴. In spite of this, and their admission that the simple Waugh-Fessenden-Johnson-Bovey models have considerable predictive ability, these authors maintain that, unlike the multipolar formalisms they are proposing, these dipolar models "... have no sound theoretical basis and may not remain the formalism of choice after more data on susceptibility anisotropies become available".^{256b}

This work has shown²⁵⁴ that isotropic magnetic-shieldings at points (R, θ, ϕ) further from a molecular origin than the most-distant part of the molecular electron-density are described by the multipole expansion

$$\sigma = \sum_{L=M}^{\infty} \sum_{M=0}^L (A_{LM} \cos M\phi + B_{LM} \sin M\phi) P_L^M(\cos \theta) / R^{L+1} \quad (1.135)$$

It has also shown²⁵⁶ that shieldings at points (r, θ, ϕ) closer to an arbitrary origin than the nearest region of molecular electron-density are conveniently calculated by use of the expansion

$$\sigma = \sum_{L=0}^{\infty} \sum_{M=0}^L (F_{LM} \cos M\phi + G_{LM} \sin M\phi) r^L P_L^M(\cos \theta). \quad (1.136)$$

In both expansions, the angular dependence of the shielding is determined by the associated Legendre-polynomials, $P_L^M(\cos \theta)$; the coefficients A_{LM} , B_{LM} , F_{LM} and G_{LM} measure anisotropy in the multipolar magnetic-susceptibilities of the functional group responsible for the shielding.

Stiles has also demonstrated²⁵⁵ that these expressions may be simplified for magnetic shielding associated with symmetrical functional-groups. There are, however, difficulties in obtaining rigorous multipolar-expansions in spherical harmonics for isotropic shielding near non-spherical groups; these authors²⁵⁴⁻²⁵⁶ have therefore suggested that expansions of the isotropic shielding in ellipsoidal harmonics may provide a more-general solution to this problem for groups which are ellipsoidal in shape. Using such an approach, Stiles has derived the following results for the dipolar contributions to isotropic shielding with an axially-symmetric group.

$$\sigma^{(N)} = \frac{1}{a_o^3} (\chi_{\parallel} - \chi_{\perp}) \left[\frac{1}{2} \ln \left(\frac{U+1}{U-1} \right) - \frac{U}{U^2 - V^2} \right] \quad (1.137)$$

(for the prolate molecular-shape) and

$$\sigma^{(N)} = \frac{1}{a_o^3} (\chi_{\parallel} - \chi_{\perp}) \left[\tan^{-1} \left(\frac{1}{U} \right) - \frac{U}{U^2 + V^2} \right] \quad (1.138)$$

(for the oblate molecular-shape). In (1.137) and (1.138), U and V are confocal, spheroidal co-ordinates, and $\chi_{\parallel}$ and $\chi_{\perp}$ are parallel- and perpendicular components of the magnetic-susceptibility tensor associated with the axially-symmetric group. Stiles²⁵⁵ has illustrated the advantages of these ellipsoidal expansions by comparing their predictions with those of the Pauling "ring-current" model¹ for benzene; by use of this model, the shielding at any point on the axis through the centre of the ring may be evaluated exactly and compared with the results of the dipolar expression (1.138), and of McConnell's equation (1.139) (to which both (1.137) and (1.138) tend as $U \rightarrow \infty$)

$$\sigma^{(N)} = -\frac{1}{3} (\chi_{\parallel} - \chi_{\perp}) (3 \cos^2 \theta - 1) / R^3 \quad (1.139)$$

The error due to the spheroidal approximation (equation (1.138)) was shown

to range from some 0.4% at 10 ring-radii from the ring centre to 48% at 0.5 ring-radii from the ring centre, while the corresponding errors, at these same distances, due to the spherical approximation (equation (1.139)) were 1.6% and 1020%, respectively.

1.6 Criticisms of the "Ring-Current" Concept

In view of the extent of the discussion so far outlined about the "ring-current" effect and the multifarious theories of it (§1.1 - 1.5), it is perhaps an understatement to say that the "ring-current" idea is one which has firmly established itself and gained wide acceptance in all branches of Chemistry. There have, however, been a few quite-vehement attacks on the concept^{81,257,258}, in the Literature; it has, on the other hand, been equally strongly defended^{259-261,158,41,236} and, although the controversy which ensued is now somewhat passé, we briefly review, in this subsection, the arguments for and against the "ring-current" concept. The present writer has commented on this controversy in more detail elsewhere¹¹¹ — an account on which we draw freely in this subsection.

The late J.I. Musher, in particular, has disputed^{81,257} the legitimacy of making a σ - π separation and then of treating the π -electrons as a special case because of the 'mobility' which they allegedly have on account of their 'delocalisation'. Musher accused London (somewhat ungraciously, perhaps, since London himself had, by this time, been dead for a decade!) of only accepting the solutions afforded by what Musher called "guessed-at" GIAO-basis-sets because they corresponded to "... his preconceived notions ... that the mobile electrons provide 'ring currents'."^{81b} Musher claims that local diamagnetic-anisotropy can account for magnetic susceptibility and ¹H-NMR

shifts in both benzene* and cyclohexane and that "ring currents" are "a fiction"²⁵⁷; the notion that 'delocalisation' plays any part in these effects is also condemned by Musher as being only "... artefact of London's approximate calculation".

A somewhat esoteric argument then ensued in the pages of the Journal of Chemical Physics between Musher^{81a,257}, and Gaidis and West²⁵⁹. The latter authors maintained that Musher^{81a} had shown only that the susceptibility of electrons on a localised model is unaffected by antisymmetrisation and had still not compared a 'local' model to one in which the electrons are "physically delocalised around the ring". Gaidis and West²⁵⁹ also made the apparently unassailable point that Musher's 'localised' model could not account for the very high-field ¹H-NMR shifts observed in the porphyrins. Musher, however, deflected this criticism with the somewhat naïve (and philosophically incorrect**) statement that the arguments he has put forward "... represent an anti-theory in that they show the generally accepted ring-current theories to be invalid and such an anti-theory, by its very nature, cannot be refuted by experiment no matter how seemingly devastating". This kind of polemic has not convinced many authors.

Hameka²⁵⁸ and Pople²⁶⁰ have also had a dispute in the Journal of Chemical Physics, although a much less acrimonious one, about the assumptions in "ring-current" theory of which Pople^{131,263} has made much use in his quest for a general theory of diamagnetism¹¹¹. Hameka's criticisms²⁵⁸, and some of those of Musher,^{81b} have centred on the neglect of certain

* An attempt by Musher to account similarly for the ¹H-NMR shifts of a wide range of condensed, benzenoid hydrocarbons published by the present author at the end of the 1960's^{60,174} (and adequately rationalised¹⁴⁰ on the basis of the McWeeny "ring-current" theory¹³² (§1.4(i)(i)) and later by other "ring-current" theories (see §1.4(ii)(b) and Chapters II and III)) did, however, on Musher's own admission²⁶², fail entirely; (the late J.I. Musher²⁶², personal communication, York, 1970).

** I am indebted to my philosophy colleague, Mr. O.P. Wood (Christ Church), for helpful clarification and discussion on this point.

integrals which occur in the "ring-current" theory. Pople²⁶⁰ has attempted to counter these points by emphasising that the value of quantum-mechanical theories in large molecules should not always be judged by the numerical accuracy of their approximations, for there are many examples of mathematically crude theories which have led to useful qualitative and semi-quantitative concepts.

Musher^{81b} has specifically criticised the neglect of terms in A_j and A_j^2 in equation (1.37). The present writer¹¹¹ has concurred with Pople²⁶⁰ that integrals such as

$$\int \phi_i^{(o)*} (\tilde{A} - A_j)^2 \phi_j^{(o)} d\tau \quad (1.140)$$

represent intra-atomic terms. Because these integrals are associated with the empirical atomic-terms, the zero of energy in the secular equations is taken to be α ($= H_{ii}$ from equation (1.37)). As Salem²⁰, and the present author¹¹¹, have pointed out, if the local contribution to the change in the total energy were of interest, it would be important to account for the difference $(\alpha - \alpha^{(o)})$, where $\alpha^{(o)}$ is the ordinary Hückel Coulomb-integral in the absence of the external magnetic-field (see §1.4(i) (e)). The present writer has stated his belief¹¹¹ that Musher's objections⁸¹ to neglect of integrals such as (1.140) are merely a further aspect of his more-basic objection to splitting the magnetic susceptibility into 'local' and 'delocalised' contributions. Pople and Ferguson,^{242,264} and Dailey¹²², and others have, in fact, discussed the likelihood that there are important localised anisotropic-contributions to susceptibilities in addition to "ring-current" contributions; the present writer has put on record¹¹¹ his opinion that Musher's argument⁸¹ is essentially that these two contributions are one and the same.

Nowakowski¹⁵⁸ appears to be the only other author actually to have used Musher's 'increment'-method⁸¹; he calculated the diamagnetic anisotropy of ten benzenoid hydrocarbons by the London theory³, by the London

method based on an HMO self-consistent with respect to bond length, by Guha and Basu's empirical correlation²⁶⁵ with HMO bond-bond polarisabilities, and by Musher's method.⁸¹ The conclusion of Nowakowski's investigation¹⁵⁸ was that the London theory based on a self-consistent LCAO-MO is in best agreement with experiment, whatever experimental set of data is compared with, thus apparently invalidating Musher's claim⁸¹ that the latter's 'increment' method could reproduce experimental anisotropy more closely than was possible via any theoretical approach based on the concept of "ring currents".

Another interesting, and distinctly 'anti-Musher,' paper was published by Kumanova and Rebane²⁶¹ in 1971. They considered the experimental values^{72,266,267} for the mean molar-susceptibilities, ($\bar{\chi}$), of four series of cyclic hydrocarbons, containing $m = 5, 6, 7$ or 8 carbon atoms.

$m = 5$: cyclopentane, cyclopentene, cyclopentadiene

$m = 6$: cyclohexene, cyclohexane, 1,3 cyclohexadiene, benzene

$m = 7$: cycloheptane, cycloheptene, 1,3 cycloheptadiene, 1,3,5 cycloheptatriene.

$m = 8$: cyclooctane, cyclooctene, 1,3 cyclooctadiene, 1,3,5 cyclooctatriene cyclooctatetraene.

A plot of the dependence of the diamagnetic susceptibility of these hydrocarbons* (in which m is the number of carbon atoms) on the number of double bonds, n , in the ring, is shown in Figure 1.8.

In each of the four series, the appearance of a new double-bond in the ring produces an almost linear change in $\bar{\chi}$; the cases where n attains its maximum value ($n=2$ for a five-membered ring, $n = 3$ for six- and seven - membered ones) are exceptions. In particular, a sharp jump in

* In cgs units.

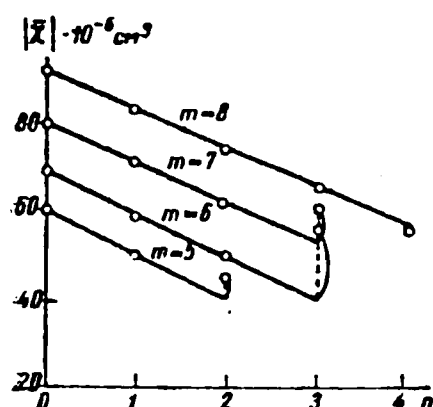


FIGURE 1.8

the susceptibility is clearly visible in the transition from cyclohexadiene to benzene. Kumanova and Rebane²⁶¹ conclude: "The sole reason for such a jump in the susceptibility is a ring current due to the π -electrons."

The series terminating in cyclooctatetraene, on account of the latter's non-planar structure (which is therefore presumably unable to support a "ring current"), does not show any discontinuity in the trend of its susceptibilities. These authors also estimated the contribution of local anisotropy of bonds and atoms to the total diamagnetic-anisotropy of benzene to be ca. 25% — close to the theoretically-calculated values of Caralp and Hoarau,^{203a} and Pople²⁴².

Finally, a very-recent analysis by Gomes²³⁶ has questioned the validity of Musher's argument in ref. 81a in which, in building up his 'localised' model for benzene, Musher divides the benzene ring into four, ostensibly-discontinuous, quadrants. Gomes has maintained that the assumptions which Musher made concerning discontinuities, or otherwise, at the boundaries of these quadrants require closer examination^{236,268} than the somewhat cursory introduction they were given in ref. 81a.

In the late 1960's, and until the early 1970's, most authors in this field seemed to feel obliged at least to make reference to the "ring-current" controversy of Musher,^{81,257} and Gaidis and West²⁵⁹. Most, however, having done so, then proceeded conveniently to disregard it. These

days, in the current Literature, the subject is hardly mentioned. The consensus has adopted the view of Gaidis and West²⁵⁹ that "... it would be unwise to discard the ring-current model, which has worked so well in numerous instances, unless a new model can lead to more-accurate predictions. Ring currents continue to provide the only satisfactory explanation for the large diamagnetic-shift of protons inside, or immediately above, an aromatic ring". These authors also maintain that "the agreement he [Musher] obtained without ring currents is not sufficient reason to deny their existence".²⁵⁹ The present writer¹¹¹ has cautioned, however, that "... the fact that predictions of 'ring-current' theory may compare favourably with experiment ... is likewise no 'proof' that 'ring-currents' do 'exist!'"¹¹¹

1.7 Other Contributory Factors to ¹H-NMR

Chemical-Shifts of Conjugated Systems

When comparing theoretical and experimental ¹H-NMR shifts in conjugated systems we shall have to take into account two other effects which, in spite of some recently-expressed doubts¹²⁵, are generally agreed to contribute to the low-field shifts of the protons in conjugated molecules: these are 1) contributions from the anisotropy of the sigma bonds,^{120-122,269,270,140} and 2) downfield shifts from van der Waals dispersion-interactions^{271,272} between sterically overcrowded protons.^{273,274,120,170,171,140}

In one of the most systematic investigations of these effects, Haigh et al.¹⁴⁰ have shown that chemical-shift contributions from the anisotropy of magnetic susceptibility of the C-C and C-H sigma-bonds in benzenoid hydrocarbons vary very little between a benzene proton and protons in a general, polycyclic, benzenoid molecule; sigma-bond anisotropies are thus not important in determining the relative proton-chemical-shifts

in such molecules, even though the absolute contribution from these effects may, in fact, be considerable. These authors¹⁴⁰ have also shown, both by direct calculation²⁷² and, empirically, by subtracting a calculated "ring-current" contribution from observed chemical-shifts, that the van der Waals contribution to the downfield shift of a pair of H α 3 protons (Martin's nomenclature²⁴¹) — such as the overcrowded protons in phenanthrene — is ca. 0.6 ppm. Haigh and the present author³⁸ have also considered that part which van der Waals effects play in the ^1H -NMR shifts of the overcrowded H α 4, H α 5 and H α 6 protons²⁴¹ which are encountered in the helicenes.

1.8 Aims of the Present Work

These fall into four main categories:

- 1) To review, in a critical and considered way, the historical development of the "ring-current" effect. This has been done in the present Chapter which, because of the writer's desire to be critical and detailed (particularly in that which concerns the London-McWeeny method^{3,132} much used in later chapters), is considerably longer than is customary in thesis introductions. This is intentional; for the present author does not wish Chapter I to be merely a comprehensive (although, it is hoped, almost complete^{*}) catalogue of previous papers in the field which will serve as an introduction to the new work to be described in the Thesis — proper; it is primarily intended to be a record of the writer's own critique of those areas of the subject on which he has felt able to express a considered opinion, based on many years in this field, and on discussions and correspondence he has benefitted from during this period with most of the leading figures in it.
- 2) To assess the empirical utility of simple theories of the "ring-current" effect by confronting their predictions with accurate and consistent experimental ^1H -NMR chemical-shift data on the alternant, condensed, benzenoid hydrocarbons.

* See Appendix E

- 3) To use the mathematical techniques of graph theory in order to investigate the topological aspects of simple "ring-current" calculations on conjugated systems; and to exploit these topological considerations in order to rationalise the relative magnitudes of "ring-current" intensities calculated, on the basis of the London-McWeeny method, in arbitrary conjugated-hydrocarbons.
- 4) To consider the success of "ring-current" approaches, of varying degrees of sophistication, when applied to calculate intra-molecular "ring-current" effects in certain non-alternant hydrocarbons and strongly-paramagnetic, conjugated systems.

1.9 Form of Presentation of the Thesis

Consistent with the aims of the work described in the last sub-section, this Thesis will be divided into the following five parts

- Part One - Introduction: Historical and Critical Review of the "Ring-Current" Effect (Chapter I).
- Part Two - Empirical Appraisal of Simple Theories of the "Ring-Current" Effect (Chapters II to IV)
- Part Three - Topological Aspects of Simple "Ring-Current" Calculations and Rationalisation of Relative "Ring-Current" Sizes. (Chapters V to VII).
- Part Four - Non-Alternant Hydrocarbons and Strongly-Paramagnetic Conjugated Systems. (Chapter VIII).
- Part Five - General Conclusions (Chapter IX)

PART TWO

EMPIRICAL APPRAISAL OF SIMPLE
THEORIES OF THE "RING-CURRENT"
EFFECT

CHAPTER II

AN EMPIRICAL REASSESSMENT OF THE SEMI-CLASSICAL "RING-CURRENT" THEORY DUE TO WAUGH AND FESSENDEN AND JOHNSON AND BOVEY

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CHAPTER II

AN EMPIRICAL REASSESSMENT OF THE SEMI-CLASSICAL "RING-CURRENT" THEORY

DUE TO WAUGH AND FESSENDEN AND JOHNSON AND BOVEY*

2.1 Summary and Scope of the Chapter

In this Chapter we shall test the semi-classical theory of Waugh and Fessenden¹⁵, and Johnson and Bovey¹¹⁷ (predicting the effect of π -electron "ring-currents" on the secondary magnetic-fields at protons in molecules containing benzenoid rings) against a set of modern, accurate, experimental proton-chemical-shifts in a wide range of planar, alternant, benzenoid hydrocarbons. It will be shown that this theory overestimates the "ring-current" deshielding of coplanar protons in such molecules. The empirical nature of the theory will be discussed, and it transpires that when the calculated shifts are suitably scaled, correlations with observed τ -values are obtained which are as good as those found when the "ring-current" shifts are calculated from the McWeeny MO-theory¹³²; these correlations will then be used to make empirical estimates of the contributions from steric effects to the chemical shifts of the overcrowded protons in these molecules. The conclusion of the investigation reported in this Chapter is that whilst there is some theoretical justification for this scaling of the predictions from the semi-classical theory, the procedure must be considered as being essentially empirical.

2.2 Background

It has previously been shown¹⁴⁰ that McWeeny's completely quantum-

* The material reported in this Chapter has been published. The full reference is:

R.B. MALLION, "The π -Electron 'Ring-Currents' and Proton Chemical-Shifts in Planar, Condensed, Benzenoid Hydrocarbons: an Empirical Reassessment of the Semi-Classical Theory", J.Chem.Soc. (B), 1971, pp.681-686. (See also Addendum on the last page (unnumbered) of the 'Index Issue' (No. 13, 1971)).

mechanical treatment¹³² of the "ring-current" effect in planar, condensed, benzenoid hydrocarbons gives rise to a very satisfactory correlation with a set of accurate, experimental proton-chemical-shifts obtained under consistent conditions of solvent and concentration^{60,174}. In view of the availability of this large number of accurate chemical-shifts, it is of interest to use these data to reassess the reliability of the earlier, semi-classical theory of the "ring-current" effect^{15,117}; this is of particular relevance as the semi-classical theory, in the form of the tables of Johnson and Bovey^{117,118}, is still widely used by organic chemists* to estimate the shielding contributions due to the anisotropy of benzenoid rings in complex organic-molecules. In this investigation we shall not be considering chemical-shift contributions from the anisotropy of magnetic susceptibility of the C-C- and C-H- bonds in these hydrocarbons, for the size of these contributions has been shown^{140,120-122} to vary very little between a benzene proton, and protons in a general, polycyclic, benzenoid molecule; σ -bond anisotropies are thus not important in determining the relative proton-chemical-shifts in such molecules, even though the absolute contribution from these effects may, in fact, be considerable.**

2.3 The Semi-Classical Waugh-Fessenden-Johnson-Bovey Theory

Waugh and Fessenden¹⁵ and Johnson and Bovey¹¹⁷ improved the original, completely-classical, "ring-current" theories of Pauling¹ and Pople⁶ by making allowance for the fact that the π -electrons are not to be found in the plane of a conjugated molecule but have a maximum probability of being at some distance, p , above and below the molecular plane. In their theory, p

* See footnote on page 19

** This statement has been disputed in an important article by Barfield et al.¹²⁵ who claim that 'local anisotropic-effects' are important contributors to the relative proton-shieldings in benzenoid hydrocarbons. Ref. 125 was published after the work described in this Chapter, and a critique of it will be found in Appendix B.

is taken to be an empirical parameter, and since previous work¹⁵ had suggested that the "ring-current" contribution to the downfield shift of a benzene proton is ca. 1.5 p p m , p was adjusted so that the theory predicted this value for $\Delta\sigma_{\text{benzene}}^{\text{"ring-current"}}$; the value of p so found (0.064nm) was then to be used in all subsequent calculations.

Because of errors in the original paper of Waugh and Fessenden^{15a} and ambiguity about the corrections offered later^{15b}, confusion has arisen^{275,111} about the form of the final equation arising from the Waugh-Fessenden-Johnson-Bovey approach. By going back to the first principles of the calculation, and using classical electromagnetic-theory¹¹⁹, it has been shown¹¹¹ that the correct form of the final equation of this semi-classical theory is the one given by Johnson and Bovey¹¹⁷. This is embodied in equation (2.1)

$$\Delta\sigma_{sc} = \frac{\mu_0}{4\pi} \frac{ne^2}{6\pi m a} \frac{1}{[(1 + \rho')^2 + (z')^2]^{\frac{3}{2}}} \left[K(k') + \frac{1 - (\rho')^2 - (z')^2}{(1 - \rho')^2 + (z')^2} E(k') \right] \quad (2.1)$$

where $\Delta\sigma_{sc}$ is the shielding provided by n electrons circulating in a loop of radius a, at a point with cylindrical co-ordinates $(\rho'z')$, with respect to the centre of the current 'loop'; k' is the modulus of the Complete Elliptic-Integrals K and E, given by equations (2.2),(2.3a) and (2.3b)

$$k' = \left(\frac{4\rho'}{(1+\rho')^2 + (z')^2} \right)^{\frac{1}{2}} \quad (2.2)$$

$$K(k') = F(k', \frac{\pi}{2}) = \frac{\pi}{2} \left[1 + \left(\frac{1}{2}\right)^2 (k')^2 + \left(\frac{3}{2 \cdot 4}\right)^2 (k')^4 + \left(\frac{3 \cdot 5}{2 \cdot 4 \cdot 6}\right)^2 (k')^6 + \dots + \dots \right] \quad (2.3a)$$

$$E(k') = E(k', \frac{\pi}{2}) = \frac{\pi}{2} \left[1 - \left(\frac{1}{2^2}\right) (k')^2 - \left(\frac{3^2}{2^2 \cdot 4^2}\right) \frac{(k')^4}{3} - \left(\frac{3^2 \cdot 5^2}{2^2 \cdot 4^2 \cdot 6^2}\right) \frac{(k')^6}{5} - \dots - \dots \right] \quad (2.3b)$$

In benzene, where the six π -electrons can be

thought of as being in two current-'loops', distance p above and below the ring plane, equations (2.4) are applicable

$$\Delta\sigma_{sc} = \frac{3e^2}{6\pi m a} \frac{\mu_0}{4\pi} \left[\frac{1}{[(1+\rho)^2 + (z-p)^2]^{\frac{1}{2}}} \left\{ K(k_-) + \frac{1-\rho^2-(z-p)^2}{(1-\rho)^2 + (z-p)^2} E(k_-) \right\} + \right. \\ \left. \frac{1}{[(1+\rho)^2 + (z+p)^2]^{\frac{1}{2}}} \left\{ K(k_+) + \frac{1-\rho^2-(z+p)^2}{(1-\rho)^2 + (z+p)^2} E(k_+) \right\} \right] \quad (2.4)$$

$$k_- = \left(\frac{4\rho}{(1+\rho)^2 + (z-p)^2} \right)^{\frac{1}{2}} \quad (2.4a)$$

$$k_+ = \left(\frac{4\rho}{(1+\rho)^2 + (z+p)^2} \right)^{\frac{1}{2}} \quad (2.4b)$$

where (ρ, z) are now the cylindrical co-ordinates of the proton in question, relative to the ring centre (and not the centre of the current 'loop' as were (ρ', z') previously). When a general polycyclic-hydrocarbon is considered, in which the "ring-current" intensity in ring i is J_i times the benzene value, each ring contributes additively to the chemical shift of a given attached-proton, so that equation (2.1) becomes¹²² (2.5),

$$\Delta\sigma_{sc} = \frac{3e^2}{6\pi m a} \frac{\mu_0}{4\pi} \sum_i J_i \mathcal{K}(\tilde{r}_i) \quad (2.5)$$

$$\mathcal{K}(\tilde{r}_i) = \frac{1}{[(1+\rho_i)^2 + (z_i-p)^2]^{\frac{1}{2}}} \left\{ K(k_-^i) + \frac{1-\rho_i^2-(z_i-p)^2}{(1-\rho_i)^2 + (z_i-p)^2} E(k_-^i) \right\} + \\ \frac{1}{[(1+\rho_i)^2 + (z_i+p)^2]^{\frac{1}{2}}} \left\{ K(k_+^i) + \frac{1-\rho_i^2-(z_i+p)^2}{(1-\rho_i)^2 + (z_i+p)^2} E(k_+^i) \right\} \quad (2.6)$$

$\mathcal{K}(r_i)$ is a purely geometric factor, the magnitude of which, determined solely by molecular geometry, is a measure of the effect which the "ring current" in ring i of the molecule has on the secondary field at the proton under test (this proton being related by the centre of ring i by the distance r_i , specified by the cylindrical coordinates ρ_i and z_i). In equation (2.6), k_-^i and k_+^i are defined in a way analagous to that in which k_- and k_+ were defined in equations (2.4a) and (2.4b), but with ρ and z replaced by ρ_i and z_i , respectively.

For all the planar benzenoid-molecules considered in this Chapter all protons do, of course, lie in their respective molecular-planes; in all these cases, therefore, $z_i = 0$, $k_+^i = k_-^i (= k^i$, say), and since¹¹⁷ $p = 0.45902$,* $p^2 = 0.21074$, so that, in these coplanar cases only, we have equation (2.7),

$$\mathcal{K}(r_i) = \frac{2}{[(1+r_i)^2 + 0.21074]^{\frac{1}{2}}} \left[K(k^i) + \frac{1-r_i^2 - 0.21074}{(1-r_i)^2 + 0.21074} E(k^i) \right] \quad (2.7)$$

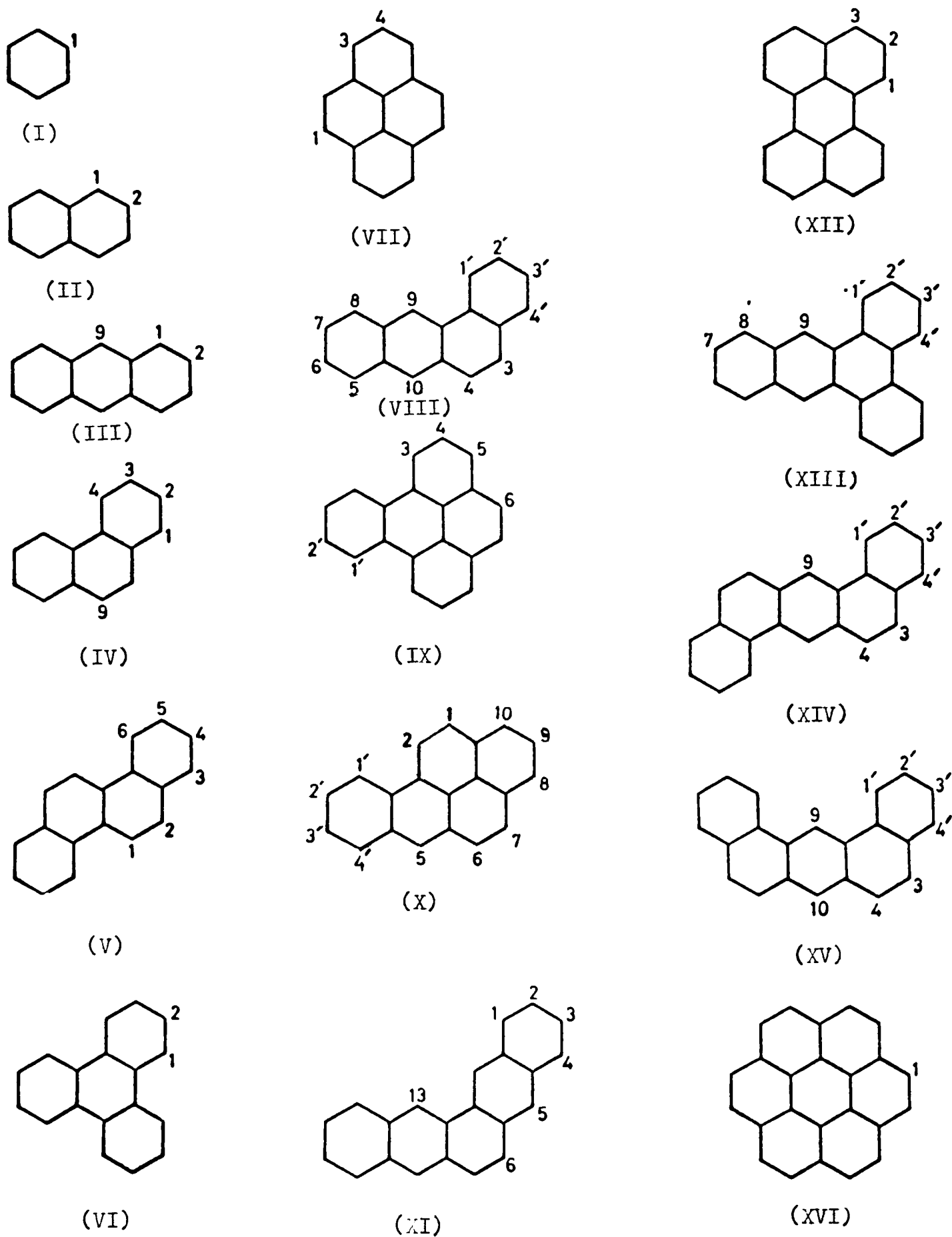
where r_i is now simply the distance, in the molecular plane, from the centre of ring i to the coplanar proton under test. The moduli of the Complete Elliptic-Integrals, K and E , are now k^i (equation (2.8))

$$k^i = \left(\frac{4r_i}{(1+r_i)^2 + 0.21074} \right)^{\frac{1}{2}} \quad (2.8).$$

and hence, by using (2.7) and (2.8), the expression for $\Delta\sigma_{sc}$ (equations (2.5) and (2.6)) simplifies accordingly.

* Here, p is expressed in units of benzene carbon-carbon bond-length (0.139 nm), as is convenient throughout all these calculations.

FIGURE 2.1



Nomenclature of Planar, Condensed, Benzenoid Hydrocarbons Studied
in this Chapter, and in Chapters III and IV

2.4 Calculations

Equations (2.5) and (2.7) were applied to the 16 condensed, benzenoid hydrocarbons for which accurate chemical-shift data are available^{60,174}. The "ring-current" intensities, J_i , were already known^{116,111,120,140} having been calculated by the method of McWeeny¹³² or the equivalent method of Pople^{131*}. Some of the geometric factors, $\mathcal{K}(r_i)$, could have been obtained from the tables of Johnson and Bovey¹¹⁸ but most of those required for the larger molecules considered were outside the range of the published tables, and so all the required $\mathcal{K}(r_i)$ -factors were here calculated directly from equation (2.7), using the Oxford-University KDF-9 computer, and tables of Complete Elliptic-Integrals²⁷⁶. The results are presented in Table 2.1, column 1, as shielding contributions, in ppm, due to the "ring-current" effect. The nomenclature of compounds, and proton numbering, follow refs. 140, 60, 174 and are detailed in Figure 2.1. For possible future reference, the individual geometric-factors, $\mathcal{K}(r_i)$, (which are intermediate numbers in the calculations obtained via equation (2.7)) are listed in Table 2.2. The left-hand column gives the geometric relation between a particular proton and that ring from the centre of which this proton is separated by the distance r_i . For example, "1,2;3,4 dibenzanthracene 3'" implies the instruction to take the origin at proton 3' in 1,2;3,4 dibenzanthracene and then to substitute in equation (2.7) the distance, r_i , between this origin and that ring in 1,2;3,4 dibenzanthracene which is most distant from it.

* The approach of this Chapter (and that of ref. 120) is aptly termed "semi-classical" for we are using Pauling's classical model¹ to calculate the absolute magnitude of the benzene "ring-current", and are then using a quantum-mechanical method (that of Pople¹³¹ or McWeeny¹³²) to estimate the "ring-current" intensities in the various rings of a general polycyclic-molecule, as a ratio (J_i) to the "ring-current" intensity in benzene. In effect, therefore, since all the J_i of equation (2.5) are here calculated from MO-theory, we are, in comparing the predictions of equation (2.5) with those from equation (1) of ref. 140, basically testing whether it is better to calculate the geometric factors (i.e., the $\mathcal{K}(r_i)$ -terms of equation (2.5)) from a classical procedure (as is done here) or from a quantum-mechanical procedure (as was done in ref. 140).

Provided that the necessary "ring-current" intensities were available, these geometric factors could then be used, if required, to calculate shieldings in other benzenoid-hydrocarbons, not considered here, in which similar geometric-relationships occur (though, in general, in different combinations) between rings and peripheral protons. (For complete details, see ref. 111, pp47-51).

2.5 Discussion

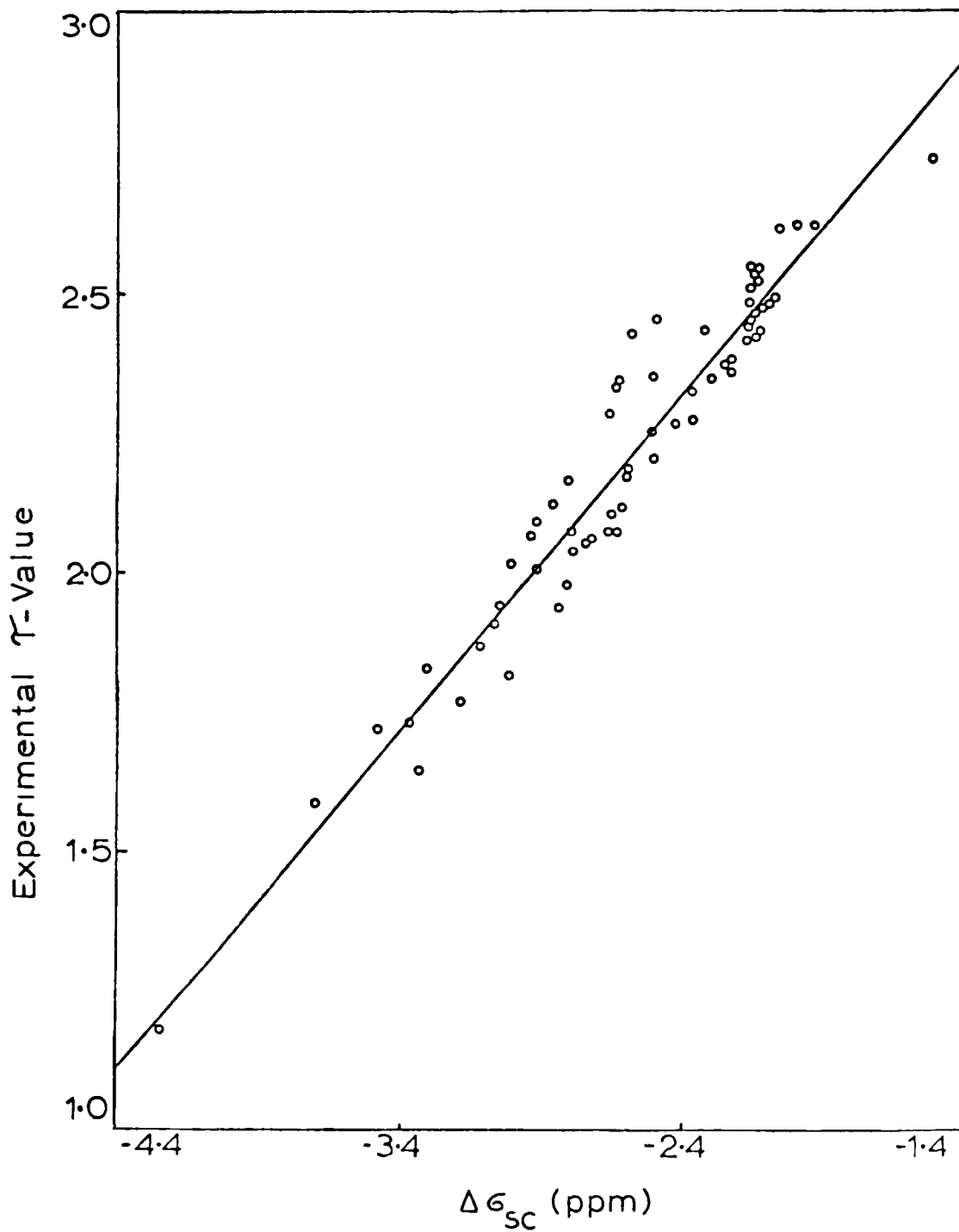
(i) The Non-hindered Protons.

We shall examine first the 66 protons considered which are not subject to gross steric-overcrowding, for previous work^{111,140,120,163,170,171} indicates that for these protons the "ring-current" effect is the major factor determining their relative chemical-shifts.

In correlating quantities derived from the McWeeny MO-theory¹³² with experimental τ -values for non-hindered protons, it was specifically emphasised¹⁴⁰ that benzene was not singled out in any way from the protons in other benzenoid-molecules for any kind of special treatment in the correlation; the calculated and experimental chemical-shifts for the benzene proton were merely the data for one point, amongst many, on an empirical regression-curve. In the semi-classical theory, however, by varying the parameter p to make the theory give the required predictions for benzene, we have immediately attributed a special status to benzene, in making it the 'reference' molecule for calibration of the theory. Having made this appeal to experiment, however, it might reasonably be expected that shifts in other benzenoid-molecules would be correctly predicted. This being the case, one would expect a straight-line relationship, with a gradient of unity, between experimental chemical-shifts^{60,174} (τ_{obs} ; Table 2.1, column 2) and shielding calculated from equations (2.5) and (2.7) ($\Delta\sigma_{\text{sc}}$; Table 2.1, column 1). However, the relation between τ_{obs} and $\Delta\sigma_{\text{sc}}$ for the 66 protons listed in Table 2.1 is (2.9),

FIGURE 2.2

Experiment-vs.-Theory Regression-Line (Equation (2.9))
with $\Delta\sigma_{sc}$ -Values Calculated via the Waugh-Fessenden-Johnson-
Bovey Method (as Detailed in Equations (2.5), (2.7) and
(2.8))



$$\tau_{\text{obs}} = 0.597(\Delta\sigma_{\text{sc}}) + 3.744 \quad (2.9)$$

(this regression line is shown in Figure 2.2) or, if shifts downfield of benzene are considered, (2.10),

$$(\tau_{\text{obs}} - \tau_{\text{obs}}^{\text{benzene}}) = 0.597(\Delta\sigma_{\text{sc}}^{\text{benzene}} - \Delta\sigma_{\text{sc}}) - 0.118 \quad (2.10)$$

which is in a form easily comparable with the very similar correlation, (2.11),

$$(\tau_{\text{obs}} - \tau_{\text{obs}}^{\text{benzene}}) = 0.63 (\Delta\sigma_{\text{sc}}^{\text{benzene}} - \Delta\sigma_{\text{sc}}) - 0.13 \quad (2.11)$$

obtained by Dailey¹²² from data for only 15 protons. In equations (2.9) and (2.10), the standard error in the slope is 0.02 ppm (3.5%), the correlation coefficient is 0.96, and the r m s -deviation for all the 66 protons listed in Table 2.1 is 0.078 ppm. When the same experimental data^{60,174} were previously regressed¹⁴⁰ against quantities derived from McWeeny's entirely quantum-mechanical theory¹³², the correlation coefficient was again 0.96, the standard error in the slope of the resulting line being 3.8% and the total r m s -deviation 0.085 ppm¹⁴⁰. Hence, over this wide range of molecules, the $\Delta\sigma_{\text{sc}}$ -quantities calculated from the semi-classical "ring-current" theory appear to correlate as well with observed τ -values as do the 'sigma ratios'¹⁴⁰ (B'/B'_{benzene}) calculated from MO-theory. In Table 2.1, therefore, τ -values observed experimentally (column 2) are compared with those calculated (column 3) from the $\Delta\sigma_{\text{sc}}$ -values (column 1) by use of equation (2.9) for all 66 non-hindered protons considered in the regression. It can be seen that the discrepancies between these two sets of τ -values (column 4) are also of the same order of magnitude as those observed in the correlation derived by use of the McWeeny MO-theory¹³².

Too much must not, however, be read into this apparently impressive

agreement; it has involved already two appeals to experiment: (i) we have invoked an experimental estimate of the "ring-current" contribution to the chemical shift of a benzene proton (to evaluate the π -electron 'lobe'-separation, $2p$). (ii) we have then regressed the resulting $\Delta\sigma_{sc}$ -values obtained with this value of p against all the available experimental τ -values, to yield the empirical equation (2.9).

Now it has already been emphasised¹⁴⁰ that in satisfactorily correlating the quantities (B'/B'_{benzene}) calculated from the McWeeny MO-"ring-current" theory¹³², with observed τ -values, only one or the other (but not both) of these two empirical procedures is required.

Memory et al.^{170,171} have assumed a value for $\Delta\sigma_{\text{benzene}}^{\text{"ring current"}}$ and then successfully predicted the shifts of protons in other benzenoid molecules, from the McWeeny theory, whilst Haigh et al.,¹⁴⁰ without assuming anything about the "ring-current" contribution to the chemical shift of a benzene proton, have obtained a regression equation between observed τ -values and calculated McWeeny-'sigma-ratios'¹⁴⁰. (Both of these procedures, on the MO-theory, are equivalent to choosing an appropriate value of β , the "Huckel resonance-integral."¹⁴⁰).

Now the fact that the gradient of the plot of τ_{obs} against $\Delta\sigma_{sc}$ is not unity, the expected value, but about 0.6, has been suggested by Dailey¹²² to be due to the use of Pauling's value¹ (-49.5×10^{-6} cgs emu) for the 'mobile'- π -electron contribution to the diamagnetic anisotropy of benzene ($\Delta\chi_{\text{benzene}}^{\text{London}}$), in calculating the benzene "ring-current", rather than the more-recent quantum-mechanical value^{122,160,194} of ca. -30×10^{-6} cgs emu; since the ratio of these two $\Delta\chi$ -values is ca. 0.6, use of the quantum-mechanical value for the anisotropy would automatically 'scale' the $\Delta\sigma_{sc}$ -quantities by the appropriate amount, without our having to resort to empirical equations such as (2.9)-(2.11). However, as has also been pointed out,¹²² use of this new value of $\Delta\chi_{\text{benzene}}^{\text{London}}$ would, in the case of benzene itself, give rise to a value of the benzene "ring-current" shift much smaller than

1.5 ppm*. This could then possibly be taken care of by recalibrating the theory, *i.e.*, by choosing a different value for the π -electron 'lobe-separation', p ; however, previous attempts^{120,163} at varying this empirical parameter have not given rise to any definitive improvements in the predictions of the theory; besides, in order to obtain a "ring-current" shift of 1.5 ppm for a benzene proton, by using an anisotropy of -30×10^{-6} cgs emu, p must take the very low value²⁷⁷ of 0.025 nm, and in order to reproduce the more-modern estimate¹⁴⁰ of 1.56 ppm for the "ring-current" downfield shift of benzene, p must be²⁷⁷ only 0.020 nm; such low values of p strain somewhat the physical interpretation which has been put on this parameter,^{15,117} for the implication is that the total π -electron 'lobe-separation' is at most only 0.05 nm. The difficulty is that chemical-shift predictions for protons in the immediate neighbourhood of a given ring are much more sensitive to the value assumed for p than are those for the more-distant protons—this is evident from an examination of equation (2.6) where, for points near the ring, terms such as $(1-\rho_i)^2$ and $(1+\rho_i)^2$ are comparable with $(z_i-p)^2$ and $(z_i+p)^2$, whilst for more-distant points, in the ring plane (*i.e.* points for which $z_i=0$ and ρ is large), $(1-\rho_i)^2$ and $(1+\rho_i)^2$ are $\gg p^2$; in fact, in the limit, as $\rho_i \rightarrow \infty$, the shielding predicted from the semi-classical theory is independent of the finite value assumed for the π -electron 'lobe-separation' (and, as would be expected, in this limit, shielding predictions from the semi-classical theory coincide¹¹¹ with those from the completely-classical 'point-dipole' approximation⁶).

This sensitivity to the value assumed for p when considering points near ring centres is one of the more unsatisfactory features of the semi-classical theory. The best compromise is probably to admit that the quantum-mechanical

*It should, however, be borne in mind during the present discussion, that calculations^{242,177} have suggested that the 'experimental' estimate^{15,208} of about 1.5 ppm for the "ring-current" contribution to the downfield shift of a benzene proton (inasmuch as we are justified at all in speaking of such a quantity⁸¹) might, in any case, be too large.

value of $\Delta\chi_{\text{benzene}}^{\text{London}}$ appears to be more realistic than the Pauling value, as Dailey suggests¹²², but to accept the purely empirical nature of equation (2.9) for the purpose of making quantitative predictions of unknown chemical-shifts. The constant term in equation (2.9) is a further illustration of the empirical nature of this equation; in principle, this quantity represents^{15,117,140} the τ -value of some hypothetical olefinic-proton which is in the same type of σ -bond and localised- π -bond environment as an aromatic proton, but which is not subject to the effect of π -electron "ring-currents". As Waugh and Fessenden have observed¹⁵, an olefinic proton in cyclohexa-1,3-diene (resonating^{15,278} at 4.21 τ) is one of the nearest approximations to such a proton attained in practice. Now an empirical investigation based on the McWeeny MO-theory estimated¹⁴⁰ the shift of this hypothetical proton to be 4.34 τ —quite close to the aforementioned cyclohexa-1,3-diene shift—whilst the regression line from the semi-classical theory here gives 3.74 τ for this quantity; the difference between these two estimates (ca. 0.6 ppm) is seen to be about 40% of the "ring-current" downfield-shift of a benzene proton (ca. 1.5 ppm), i.e., the amount by which the semi-classical predictions have been scaled.

In spite of all these limitations, however, the semi-classical theory seems generally to be superior to the McWeeny MO-theory in predicting the relative order of proton chemical-shifts in a complex, benzenoid hydrocarbon, and only in two of the molecules studied (1,2 benzanthracene and 1,2;7,8 dibenzanthracene) is the MO-theory more successful than the semi-classical theory in this respect. This is well illustrated by the pyrene series, i.e. pyrene, 1,2 benzopyrene, and 3,4 benzopyrene. In pyrene itself, the observed order of τ -values is¹⁷⁴ $\tau_4 > \tau_1 > \tau_3$ but the Hückel-McWeeny method predicts¹⁴⁰ $\tau_1 > \tau_4$ (a shortcoming which is not, it should be noted, rectified by more-sophisticated versions of the McWeeny theory^{169,172b,203d}); the semi-classical theory, however, predicts the experimentally-observed order. Similarly, in 1,2 benzopyrene (in which we here consider only the non-hindered

protons) the MO-theory interchanges the order of one pair of protons (4 and 6) relative to the observed order, whilst the semi-classical theory again predicts the correct relative-shifts. In 3,4 benzopyrene (with 10 non-equivalent unhindered-protons) neither theory predicts the correct relative-order, but comparison of the entries for 3,4 benzopyrene in Table 2.1 with the corresponding figures in Table 1 of ref. 140 shows that the scheme of shifts predicted by the semi-classical theory is much nearer the observed order than that predicted by the entirely quantum-mechanical method.

(ii) The Overcrowded Protons.

It has been shown^{111,120,140,163,170,171} that the chemical shifts of the overcrowded protons in these molecules are considerably affected by the steric interactions in which these protons are involved* Following previous procedure,^{140,170,171} we here estimate the apparent magnitude of these steric effects on the proton chemical-shifts by subtracting the calculated "ring-current" contribution to these shifts (as obtained by computing $\Delta\sigma_{sc}$ for the proton concerned, from equations (2.5) and (2.7), and then using equation (2.9)), from the experimentally-observed τ -values; Table 2.3 shows such differences for the 19 overcrowded protons considered. Except for the case of 1,2;7,8 dibenzanthracene proton 9, which is a doubly-overcrowded proton¹⁴⁰, the $(\tau_{obs} - \tau_{\text{"ring current"}})$ -differences are in the range 0.32-0.64 ppm, with a mean value of 0.54 ppm (to be compared with a range of 0.44-0.76 ppm and a mean value of 0.62 ppm, when these quantities were assessed¹⁴⁰ from the same experimental data, but using the McWeeny MO-theory¹³² to estimate the "ring-current" contributions). As previously observed, and rationalised¹⁴⁰, the lowest $(\tau_{obs} - \tau_{\text{"ring current"}})$ -discrepancy

* For further discussion of these steric effects, including the appropriate literature, see ref. 140. But for a different point of view, see ref. 125 and the discussion of it in Appendix B.

is again displayed by perylene, proton 1, and the highest by 1,2;7,8 dibenzanthracene, proton 1'; it is thus to some extent gratifying that the semi-classical "ring-current" theory gives rise to the same qualitative pattern of apparent steric-shifts for the overcrowded protons as does the McWeeny MO-theory^{140*}. Further, as also was observed in the MO-investigation,¹⁴⁰ the doubly-overcrowded proton in 1,2;7,8 dibenzanthracene (proton 9) has, accordingly, a $(\tau_{\text{obs}} - \tau_{\text{"ring-current"}})$ -discrepancy (1.07 ppm) of about twice the average value for singly-overcrowded protons (0.54 ppm).

2.6 Conclusions

In this Chapter, we have shown:

- (1) That the semi-classical theory of "ring currents", as presented by Johnson and Bovey,^{117,118} overestimates the contribution from this effect to the proton chemical-shifts in a wide range of planar, condensed, benzenoid hydrocarbons; this conclusion bears out the initial observations of Dailey *et al.*¹²⁰⁻¹²².
- (2) That the observed τ -values for 66 non-hindered protons in 16 polycyclic hydrocarbons are related to the quantities $\Delta\sigma_{\text{sc}}$ (calculated from equations (2.5) and (2.7), or obtained via equation (2.5) and the Johnson-Bovey tables¹¹⁸) by the empirical equation (2.9).
- (3) That for the singly-overcrowded protons¹⁴⁰, the experimental τ -values are smaller than those calculated from equations (2.5), (2.7) and (2.9) by between 0.32 and 0.64 ppm. The mean value of these discrepancies, which have been attributed to steric effects,¹⁴⁰ is 0.54 ppm.
- (4) That the correlation between τ_{obs} and $\Delta\sigma_{\text{sc}}$ is as good as that found

* This same pattern is also revealed by calculations based on more-sophisticated SCF-versions^{176,179} of the McWeeny theory¹³² and on other theories.^{177,203d} See also ref. 125 and the discussion of it in Appendix B.

between τ_{obs} and the quantities (B'/B'_{benzene}) , calculated on the McWeeny MO-theory.^{132,140} However, because of difficulties in choosing a value for the 'lobe separation', $2p$, and, in particular, the sensitivity of the predictions of the semi-classical theory to the value of this empirical parameter when considering points very near a benzenoid ring, the correlation equation (2.9) is to be regarded as purely empirical, and might well have been of a different form if the quantum-mechanical value^{122,160,194} of $\Delta\chi_{\text{benzene}}^{\text{London}}$, and a different value of p , had been used. If this procedure were carried out, however, the problem of finding a suitable value of p would still be further confounded by the fact that p really should be a range, and not a unique value, if the π -electrons are to be regarded as being in a 'cloud'. However, such a restriction must be accepted as a limitation of the model, if the semi-classical theory is to be kept simple; later attempts¹²⁶ to refine the theory have certainly increased its complexity (see §1.3(v)(c)).

(5) That the slope of 0.6 in equation (2.9) has some theoretical interpretation in the observation of Dailey¹²² that the quantum-mechanical value of $\Delta\chi_{\text{benzene}}^{\text{London}}$ is ca. 60% of the classical value; however, grafting further quantum-mechanical aspects onto the semi-classical theory is clearly somewhat unsatisfactory.

It is concluded, therefore, that, at least on aesthetic grounds, the entirely quantum-mechanical theory of McWeeny¹³² is much the more satisfactory way of rationalising "ring-current" chemical-shifts in benzenoid molecules, depending, as it does, on only one empirical parameter,¹⁴⁰ the standard carbon-carbon resonance-integral, β . However, for the purely practical purpose of predicting an unknown chemical-shift, the empirical use of equation (2.9) to convert entries in the Johnson-Bovey tables,¹¹⁸ or $\Delta\sigma_{\text{sc}}$ -values estimated from equations (2.5) and (2.7), into calculated τ -values, is likely to give predictions as quantitative as those obtained from a similar empirical-equation derived from the McWeeny MO-method;¹⁴⁰ indeed, as we have seen, for the purpose of predicting the relative order of shifts, within one molecule,

the semi-classical theory may sometimes be superior. However, this discussion has shown that, in spite of its somewhat impressive predictive-powers, the semi-classical "ring-current" theory must, in the final analysis, be regarded as an essentially empirical description of chemical-shift phenomena, at least for the case of coplanar protons in planar, condensed, benzenoid molecules.

In view of these conclusions, a quantum-mechanical version of the Johnson-Bovey tables¹¹⁸ based on an extension^{111,38b} of the McWeeny method,¹³² has subsequently been made available.¹³⁸ These tables have been fully discussed in §§1.4(i)(j) and 1.4(i)(k).

TABLE 2.1

Calculated and Observed Chemical-Shifts of the Non-hindered Protons[†]

Compound [†]	Proton [†]	$\Delta\sigma_{sc}$	$\tau_{obs}^{\ddagger}$	$\tau_{calc}^{\S}$	$\tau_{obs} - \tau_{calc}$
Benzene (I)	1	-1.500	2.73	2.848	-0.12
Naphthalene (II)*	1	-2.348	2.27	2.341	-0.07
	2	-1.923	2.62	2.595	0.02
Anthracene (III)*	1	-2.645	2.07	2.164	-0.09
	2	-2.044	2.61	2.523	0.09
	9	-3.328	1.64	1.756	-0.12
Phenanthrene (IV)*	1	-2.489	2.20	2.257	-0.06
	2	-2.058	2.49	2.514	-0.02
	3	-2.110	2.43	2.483	-0.05
	9	-2.493	2.35	2.255	0.10
Chrysene (V)	2	-2.786	2.07	2.080	-0.01
	3	-2.642	2.10	2.166	-0.07
	4	-2.150	2.48	2.459	0.02
	5	-2.211	2.38	2.423	-0.04
Triphenylene (VI)*	2	-2.118	2.42	2.479	-0.06
Pyrene (VII)*	1	-2.906	2.00	2.008	-0.01
	3	-3.055	1.90	1.919	-0.02
	4	-2.619	2.07	2.179	-0.11
1,2 Benzanthracene (VIII)	2'	-2.164	2.41	2.451	-0.04
	3'	-2.079	2.47 ₅	2.502	-0.03
	4'	-2.495	2.24 ₅	2.253	-0.01
	3	-2.483	2.45	2.261	0.19
	4	-2.647	2.28	2.163	0.12
	5	-2.728	2.05	2.114	-0.06
	6	-2.122	2.53 ₅	2.476	0.06
	7	-2.133	2.53	2.470	0.06
	8	-2.797	1.97	2.073	-0.10
	10	-3 367	1.72 ₅	1.733	-0.01
1,2 Benzopyrene (IX)	2'	-2.213	2.35 ₅	2.422	-0.07
	4	-2.652	2.07	2.160	-0.09
	5	-3.044	1.93 ₅	1.925	0.01

* The calculated $\Delta\sigma_{sc}$ -values for molecules indicated thus (*), were first given in ref. 120.

† Compound nomenclature and proton numbering are as in Figure 2.1.

‡ Observed τ -values (all at infinite dilution, or very low concentration (<0.3 mole %) in CCl_4), from refs. 60 and 174. (Footnotes continued overleaf).

TABLE 2.1 (continued)

Compound [†]	Proton [†]	$\Delta\sigma_{sc}$	$\tau_{obs}^{\dagger}$	$\tau_{calc}^{\S}$	$\tau_{obs} - \tau_{calc}$
3,4 Benzopyrene (X)	6	-2.926	2.06	1.996	0.06
	1	-3.176	1.76	1.847	-0.09
	2'	-2.412	2.26	2.303	-0.04
	3'	-2.349	2.31 ₅	2.341	-0.03
	4'	-3.007	1.81	1.948	-0.14
	5	-3.704	1.58 ₅	1.531	0.05
	6	-2.914	2.09	2.003	0.09
	7	-2.804	2.16	2.069	0.09
	8	-2.998	2.01	1.953	0.06
	9	-2.601	2.11 ₅	2.190	-0.08
Pentaphene (XI)	10	-3.108	1.86 ₅	1.887	-0.02
	1	-2.826	1.93	2.056	-0.13
	2	-2.138	2.50 ₅	2.467	0.04
	3	-2.118	2.52	2.479	0.04
	4	-2.708	2.05 ₅	2.126	-0.07
	5	-3.300	1.82	1.773	0.05
Perylene (XII)*	6	-2.572	2.42 ₅	2.207	0.22
	2	-1.979	2.62	2.562	0.06
	3	-2.312	2.43	2.363	0.07
1,2;3,4 Dibenanthracene (XIII)	2'	-2.128	2.46	2.473	-0.01
	3'	-2.095	2.47	2.492	-0.02
	7	-2.141	2.54 ₅	2.465	0.08
1,2;5,6 Dibenanthracene (XIV)	8	-2.780	2.03 ₅	2.083	-0.05
	2'	-2.227	2.37 ₅	2.413	-0.04
	3'	-2.137	2.45	2.467	-0.02
	4'	-2.581	2.18	2.202	-0.02
1,2;7,8 Dibenanthracene (XV)	3	-2.620	2.33	2.179	0.15
	4	-2.854	2.12	2.039	0.08
	2'	-2.264	2.34 ₅	2.391	-0.05
	3'	-2.149	2.44	2.460	-0.02
	4'	-2.585	2.17	2.200	-0.03
	3	-2.610	2.34	2.185	0.16
	4	-2.785	2.20 ₅	2.080	0.12
	10	-3.477	1.71 ₅	1.667	0.05
Coronene (XVI)		-4.240	1.18	1.211	-0.03

[§] From equation (2.9)

|| The calibration is arranged so that $\Delta\sigma_{sc}$ for the benzene proton is 1.5ppm (see text)

Geometric Factors for the Semi-Classical Johnson-Bovey Method

Compound and Proton §	Complete Elliptic-Integrals		Geometric Factor $\mathcal{K}(r_i) \ddagger$
	$K(k^i)^*$	$E(k^i)^{\dagger}$	
Benzene (I)	2.5654	1.1070	-1.4990
Naphthalene (II) 1	2.2690	1.1751	-0.6495
2	2.0699	1.2440	-0.2607
Anthracene (III) 1	2.0013	1.2736	-0.1722
2	1.8957	1.3268	-0.0775
Phenanthrene (IV) 1 (or 3)	1.9697	1.2886	-0.1392
2	1.9174	1.3150	-0.0932
4	2.2309	1.1865	-0.5610
1,2 Benzanthracene 1'	2.0286	1.2614	-0.2050
(VIII) 2' (5)	1.8738	1.3391	-0.0635
3' (6)	1.8289	1.3660	-0.0397
4' (7)	1.8485	1.3540	-0.0497
8	1.9542	1.2961	-0.1251
Pentaphene (XI) 1	1.8793	1.3360	-0.0668
2 (4)	1.8014	1.3835	-0.0290
3	1.7796	1.3980	-0.0214
1,2;5,6 Dibenanthracene (XIV) 1'	1.8793	1.3360	-0.0668
2'	1.8014	1.3835	-0.0290
3'	1.7796	1.3980	-0.0214
4'	1.8014	1.3835	-0.0290
1,2;7,8 Dibenanthracene (XV) 1'	2.0172	1.2664	-0.1902
2'	1.8704	1.3411	-0.0611
3' (4')	1.8109	1.3773	-0.0322

* From equation (2.3a), with k^i as modulus

† From equation (2.3b), with k^i as modulus

‡ From equation (2.7)

§ Compound nomenclature and proton numbering are as in Figure 2.1.

TABLE 2.3

Calculated and Observed Chemical-Shifts (ppm) for the Overcrowded Protons*

Compound*	Proton*	$\Delta\sigma_{sc}^\dagger$	$\tau_{obs}^\ddagger$	$\tau_{calc}^\S$	$\tau_{calc} - \tau_{obs}$
Phenanthrene (IV)	4	-2.967	1.38	1.973	0.59
Chrysene (V)	6	-3.163	1.28	1.856	0.58
	1	-3.239	1.34	1.810	0.47
Triphenylene (VI)	1	-2.928	1.39	1.996	0.61
Perylene (XII)	1	-2.573	1.89	2.208	0.32
1,2 Benzanthracene (VIII)	1'	-3.205	1.23	1.831	0.60
	9	-3.841	0.92	1.451	0.53
Pentaphene (XI)	13	-3.992	0.82 ₅	1.361	0.54
1,2 Benzopyrene (IX)	1'	-3.189	1.24 ₅	1.840	0.60
	3	-3.455	1.19 ₅	1.681	0.49
3,4 Benzopyrene (X)	2	-3.679	1.02	1.548	0.53
	1'	-3.542	1.02 ₅	1.629	0.60
1,2;3,4 Dibenanthracene (XIII)	1'	-3.099	1.32 ₅	1.894	0.57
	4'	-2.870	1.52 ₅	2.031	0.51
	9	-3.718	1.03 ₅	1.524	0.49
1,2; 5,6 Dibenanthracene (XIV)	1'	-3.314	1.19 ₅	1.766	0.57
	9	-3.957	0.92 ₅	1.382	0.46
1,2;7,8 Dibenanthracene (XV)	1'	-3.456	1.04	1.681	0.64
	9	-4.439	0.02	1.094	1.07

* Proton and compound numbering as in Figure 2.1.

† In the cases of those protons considered by Jonathan *et al.*¹²⁰ (phenanthrene 4, triphenylene 1, and perylene 1), the $\Delta\sigma_{sc}$ - values given here are about 0.08 ppm larger than the previous values;¹²⁰ checking (i) by use of equations (2.5) and (2.7) and (ii) by use of the Johnson-Bovey tables¹¹⁸ favoured the values reported here.

‡ Observed τ -values from refs. 60 and 174.

§ From equation (2.9).

CHAPTER III

ON GAUGE FACTORS AND A SEMI-CLASSICAL ALTERNATIVE TO THE McWEENY 'TEST-DIPOLE' FORMALISM

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CHAPTER III

ON GAUGE FACTORS AND A SEMI-CLASSICAL ALTERNATIVE

TO THE McWEENY 'TEST-DIPOLE'-FORMALISM *

3.1 Scope and Summary of the Chapter

In this chapter we shall discuss some recent criticisms of the gauge factors which are usually employed in the 'test-dipole' method for the calculation of "ring-current" chemical-shifts in conjugated molecules. It will be shown that, in a simple semi-empirical scheme of the London-McWeeny type, insertion of a dipole contribution into the vector potential appearing in the gauge factor, whilst having no effect on the calculated "ring-current" intensities, is algebraically analogous (and, at large distances from ring centres, numerically equivalent) to estimating the secondary field at the origin due to a set of classical line-currents, as discussed originally by Longuet-Higgins and Salem^{127,20} these 'line currents' are of the same magnitude as the quantum-mechanical 'bond-currents' implicit in the "ring currents" calculated using the simpler gauge factors originally due to London, but their contributions to the secondary magnetic-field experienced by the peripheral protons are estimated classically. Extensive numerical-comparison will be made between experimentally observed proton-chemical-shifts in the same conjugated hydrocarbons as was considered in Chapter II and secondary fields estimated by this semi-classical formalism; its predictions are found to correlate as well with experiment as do those of the original McWeeny

* The material reported in this chapter has been published. The full reference is:

R.B. MALLION, "On the Magnetic Properties of Conjugated Molecules", Molec.Phys., 1973, Vol. 25, pp.1415-1432.

approach. The conclusion of the investigation reported in this Chapter is that any further illegitimacy involved in the procedure of inserting a dipole contribution into the gauge factor is evidently quite simply compensated for, numerically, by an appropriate empirical-parametrisation. Such empirical parametrisations may also absorb errors due to all the other various approximations of the "ring-current" theories (with apparently unwarranted efficiency) and it is therefore concluded that they should be treated with more scepticism than has previously been thought necessary.

3.2 Introduction

We saw in Chapter I (§1.4(i)(c)) that when a planar, conjugated molecule is placed in a magnetic field $\underline{B}_0$, the wave function ψ_0^π , describing its π -electrons in the absence of the field, is usually considered³ to be replaced by ψ^π , such that if ψ_0^π is made up of the set of LCAO-functions $\{\phi_i^{(0)}\}$, then ψ^π consists of the set of LCAO-functions $\{\phi_i\}$, where

$$\phi_i = \phi_i^{(0)} \exp \left[-\frac{2\pi i e}{h} \underline{A}_i \cdot \underline{r} \right] \quad (3.1)$$

in which $\underline{A}_i$ is the vector potential at nucleus i , due to the external field, and $\underline{r}$ is the position vector of an electron in ϕ_i . As shown in §1.4(i)(c), $\underline{A}_i$ is not uniquely determined by specifying $\underline{B}_0$ but, in the presence of a uniform, external field, the required vector-potential can be taken to be, for example,

$$\begin{aligned} \underline{A}_i &= \frac{1}{2} \underline{B}_0 \times \underline{R}_i \\ &= \frac{1}{2} \underline{B}_0 k \times \underline{R}_i, \end{aligned} \quad (3.2)$$

where $\underline{R}_i$ is the vector relating nucleus i to the arbitrary origin; in the second line of equation (3.2), $\underline{k}$ is a unit vector normal to the molecular

plane, i.e. the external, applied field, B_0 , is considered to be perpendicular to the plane of the conjugated molecule. All this follows London (see Chapter I, §1.4(i)(c)).

Now McWeeny²¹⁹ has drawn attention to the fact that, in previous theories of proton shielding (e.g. refs 132, 169, 172, 176, 192), including his own,¹³² it has been customary to modify the gauge factor in equation (3.1) by adding to $\tilde{A}_i$ a dipole contribution, $\tilde{A}_n$, due to an infinitesimal 'test' dipole, of moment $n\tilde{k}$, introduced (as an artifact) at any point in the molecular plane where we wish to evaluate the secondary magnetic-field, B' , due to the induced-current distribution in the molecule; so that the vector potential at nucleus i now becomes:

$$\tilde{A}_i = \left(\frac{1}{2} B_0 + \frac{\mu_0}{4\pi} \frac{n}{R_i^3} \right) \tilde{k} \times \tilde{R}_i \quad (3.3)$$

and this dipole contribution is thus included in the LCAO wave-function, via equation (3.1). As McWeeny has pointed out²¹⁹, however, this step is unnecessary as far as 'gauge-invariance' criteria are concerned and, even though it leads to an elegant formalism¹³² in which explicit reference to the current-density operator is avoided, this procedure is considered to be of 'doubtful validity'²¹⁹; it may be argued (somewhat heuristically) that the dipole (unlike the external field) is only an artifact of the physical system, and we have, therefore, no right to include its effect on the wave function as such — which is what we are doing by defining $\tilde{A}_i$ in equation (3.1) via equation (3.3). (In principle, however, the problem could be tackled by considering the dipole as the primary physical-influence, and the external field as the 'artifact' (see Appendix A)). McWeeny concludes, therefore²¹⁹, that what should be evaluated by first-order perturbation-theory is the coupling energy between the 'test' dipole and the required secondary-field, using, as the unperturbed wave-function,

Ψ^π , the set of $\{\phi_i\}$ defined by equations (3.1) and (3.2) — i.e. the Ψ^π which describes the molecule in the presence of the uniform, external, magnetic-field only (as, indeed, other approaches have done^{136,279,175,193}).

However, within the last decade, many calculations have been made,^{82,114,116,140,141,155,170,171,180} based on the original McWeeny 'test-dipole' approach, using equations (3.1) and (3.3) — involving the computation of relative "ring-current" intensities^{132,82,114,116,140,141,155} in conjugated molecules, and/or the estimation of secondary fields (and, hence, nuclear-screening constants) due to these "ring currents".^{132,140,141,170,171,180} It is, therefore, of interest to consider the repercussions of this recent critique²¹⁹ on the status and validity of these calculations. Hence it is the purpose of the present chapter to develop some suggestions of McWeeny¹³², Longuet-Higgins and Salem,^{127,20} and Haigh²⁸⁰ to investigate the numerical consequences, within the framework of the simple London-McWeeny method,^{3,132} of using the gauge factor defined by equations (3.1) and (3.2) instead of that defined by equations (3.1) and (3.3), the one usually used in the 'test-dipole' approaches^{132,169,172,192*}. In this assessment, we shall invoke the 'classical-line-current' concept introduced by Longuet-Higgins and Salem^{127,20}, and will show that use of such a procedure, though it has unattractive, classical features, is, in fact, not only algebraically analogous to including the dipole term in the gauge factor (as in equation (3.3)) in the entirely quantum-mechanical McWeeny-approach,^{132,20} but is also actually numerically equivalent, even when the secondary fields at points relatively close ($>3 \text{ \AA}$) to a conjugated ring are considered. Before doing this, however, since the methodology of this semi-classical theory is very much in the spirit of the entirely

* For an examination of still further consequences of this approximation, see the discussion of Parker and Memory¹⁸³.

quantum-mechanical current-density formalism^{136,279,175} we briefly discuss the latter approach (and its relation to the test-dipole method) in the next Section.

3.3 Philosophy of the Current-Density and Test-Dipole Approaches

In his original paper¹³² McWeeny used the 'test-dipole' approach, whilst Slichter¹³⁶, Pople²⁷⁹, Amos and Roberts¹⁷⁵ and, more recently, the present author with Coulson and Gomes¹⁶² have adopted the so-called 'current-density' operator; in this latter method, for an N-electron system (such as the π -electron system of a planar, conjugated molecule), if $\Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_j, \dots, \underline{r}_N)$ is an exact eigenfunction of the system in the presence of an external magnetic-field $\underline{B}_0$, but in the absence of any dipolar coupling, the current density associated with the jth electron is defined¹³⁶ (where we here consider only the space part of this uniform-field solution):

$$\underline{J}_{oj}(\underline{r}_j) = \int \left\{ \frac{\hbar e}{2mi} (\Psi \nabla_j \Psi^* - \Psi^* \nabla_j \Psi) - \frac{e^2}{m} \underline{A}_{oj} \Psi^* \Psi \right\} d\tau_1 d\tau_2 \dots d\tau_{j-1} d\tau_{j+1} \dots d\tau_N ds_j. \quad (3.4)$$

where $\underline{A}_{oj}$ is now the vector potential at electron j (due to the external field only).

First-order perturbation-theory then gives the energy of interaction with a dipole of moment $n\underline{k}$, as

$$E_{\text{dipole}} = -n\underline{k} \cdot \left[\frac{\mu_0}{4\pi j} \int \frac{\underline{r}_j \times \underline{J}_{oj}(\underline{r}_j)}{r_j^3} d\tau_j \right] \quad (3.5)$$

and, hence, if $\underline{B}'$ is the secondary field at the position of a nuclear- or 'test' dipole, due to the induced-current distribution in the molecule,

(or as Musher⁸¹ terms it, the 'pseudo-field' due to this current distribution, definable only in terms of the energy E_{dipole}), then $\underline{B}'$ is interpreted as being represented by the term in square brackets in equation (3.5), since this equation is of the form of a classical interaction between a current density, $\underline{J}_{\text{oj}}(\underline{r}_j)$, and a magnetic dipole of moment $\underline{n}^{136}$ i.e.,

$$E_{\text{dipole}} = - \underline{n} \cdot \underline{B}'. \quad (3.6)$$

Thus, the only difference in philosophy between the two approaches is that in the 'test-dipole' formalism, $\underline{B}'$ is evaluated from equation (3.6), whilst in the 'current-density' method, it is calculated from (3.5); however, provided that $\underline{J}_{\text{oj}}(\underline{r}_j)$ is an exact current-density, in the presence of the uniform field only, these are rigorously equivalent alternatives; but even when the wave function is not exact, and the $\underline{J}_{\text{oj}}(\underline{r}_j)$ can consequently no longer be strictly defined via the Schrödinger equation, (3.5) and (3.6) can still be used provided that Ψ is a variationally-determined uniform-field solution (see for example ref. 281 and Appendix A).

The point at issue here, therefore, is not the equivalence of the test-dipole and current-density approaches (which may persist even with approximate wave-functions, as we have seen), but rather the question of whether to include the dipole field in the actual definition of Ψ (as in equation (3.3)); the above considerations seem to indicate that it should not be so included, since its presence would disturb the stationary-value properties of the uniform-field solution. This, therefore, is where doubt is raised about the legitimacy of the procedure adopted in McWeeny's original 'test-dipole' paper¹³² (and refinements based on it^{169,172,176,192,38b}) but this procedure is not a feature of the test-dipole method per se (which is familiar throughout physics and is clearly satisfactory conceptually). The 'test' object should not, however, disturb the system of interest; in particular, it should leave the wave function of the system unchanged. For further

discussion of this point, the reader is referred to Appendix A.

3.4 Induced-Current Distribution Via the Framework of the McWeeny Method

We now point out another route to the familiar "ring-current" expressions,¹³² without invoking the test-dipole concept; the method does not give the induced field itself (which, quantum-mechanically, requires a further calculation of the interaction between the currents and a test dipole) and, in fact, here the secondary field is finally estimated classically, from the calculated "ring-currents"; in this way, some of the difficulties of a direct quantum-mechanical calculation are avoided.

To do this, we shall follow through the McWeeny perturbation-approach,¹³² but using equations (3.1) and (3.2) to define our LCAO-basis, instead of equations (3.1) and (3.3), the ones McWeeny used¹³². Our aim will be (a) to calculate the induced-current distribution amongst the π -electrons of the molecule, and then (b) to estimate the effect of this induced-current distribution on the secondary magnetic-field at any particular point in space in the vicinity of the molecule, by means of some appropriate (in this case, classically-calculated) geometric-factor; in other words, we shall attempt to simulate the philosophy of the current-density method, (outlined in §3.2), using the framework of the McWeeny 'test-dipole' perturbation-approach¹³² but without making explicit reference either to the test dipole or to the current-density operator.

In McWeeny's notation,¹³² these considerations determine that the i - j element of the matrix of perturbed resonance-integrals is still represented by

$$\beta_{ij} = \beta_{ij}^{(o)} \exp(i\theta_{ij}) \quad (3.7)$$

(with $\beta_{ij}^{(o)} = \eta_{ij} \beta$, β being the standard benzene Hückel-resonance-integral

— for simplicity, we assume here that all $\eta_{ij} = 1$) but θ_{ij} is now defined:

$$\theta_{ij} = 2\pi \left(\frac{e}{h} \right) S s_{ij} B_o \quad (3.8)$$

instead of

$$\theta_{ij} = 2\pi \left(\frac{e}{h} \right) S s_{ij} \left[B_o + \frac{\mu_c^n}{4\pi a^3 r_i^3} + \frac{\mu_o^n}{4\pi a^3 r_j^3} \right] \quad (3.9)$$

as would be the case if the magnetic vector-potential due to a dipole were included in the wave-function phase-factor. Here, S is the area of a standard benzene-hexagon, a the length of a carbon-carbon bond in benzene, and s_{ij} is the signed area (in unites of S) of the triangle formed by the projection of the origin (the point at which the "ring-current" secondary-field is being calculated) into the molecular plane and the atoms at the extremities of the bond $i - j$. Now, again, following McWeeny¹³², we can express the energy term of second order in the uniform field (in the absence of a test dipole) as

$$E^{(2)} = E^{(a)} + E^{(b)} \quad (3.10)$$

with

$$\begin{aligned} E^{(a)} &= -\beta \sum_{(ij)} \theta_{ij}^2 P_{ji} \\ &= -\beta \left(\frac{2\pi e}{h} \right)^2 S^2 \{B_o\}^2 \sum_{(ij)} P_{ij} s_{ij}^2 \end{aligned} \quad (3.11)$$

and

$$\begin{aligned} E^{(b)} &= - \sum_{(ij)} \sum_{(kl)} \beta \theta_{ij} \theta_{kl} \beta \bar{\pi}_{(ij)(kl)} \\ &= -\beta \left(\frac{2\pi e}{h} \right)^2 S^2 \{B_o\}^2 \sum_{(ij)} \sum_{(kl)} \beta \bar{\pi}_{(ij)(kl)} s_{ij} s_{kl} \end{aligned} \quad (3.12)$$

or,

$$E^{(2)} = - \beta \left(\frac{2\pi e}{h} \right)^2 s^2 B_o^2 (x_1 + x_2) \tag{3.13}$$

where,

$$\begin{aligned} x_1 &= \sum_{(ij)} P_{ij} s_{ij}^2 \\ x_2 &= \sum_{(ij)} \sum_{(kl)} \beta \bar{\pi}_{(ij)(kl)} s_{ij} s_{kl} \end{aligned} \tag{3.14}$$

(In (3.11) - 3.14), P_{ij} is the bond order of the i - j bond, $\bar{\pi}_{(ij)(kl)}$ is the mutual, imaginary, bond-bond polarisability between bonds $i - j$ and $k - l$, and $\bar{\pi}_{(ij)(ij)}$ is the imaginary self-polarisability of the $i - j$ bond. We can now carry through McWeeny's unitary-transformation on the basis orbitals¹³² so that only one ('circuit-completing') bond in each ring is perturbed, and write:

$$\mathcal{S}_{(\mu)} = \sum_{\textcircled{\mu}} s_{ij} \tag{3.15}$$

where $\textcircled{\mu}$ indicates an ordered sum involving all the bonds $i - j$ around the circuit which the μ th circuit-completing bond constructs; this quantity (which is independent of the origin in the molecular plane) then represents the area of the ' μ th circuit'. Then, in a notation similar to that of McWeeny's equation (5.4) of ref. 132, equations (3.14) become:

$$x_1 = \sum_{(\mu)} P_{(\mu)} \mathcal{S}_{(\mu)} \mathcal{S}_{(\mu)} = \sum_{(\mu)} P_{(\mu)} \mathcal{S}_{(\mu)} (\dots + s_p^\mu + s_q^\mu + s_r^\mu + \dots)$$

$$\chi_2 = \sum_{(\mu)} \sum_{(\nu)} \beta \bar{\pi}_{(\mu)(\nu)}^{\frac{1}{2}} [\mathcal{L}_{(\mu)}(\dots s_{\ell}^{\nu} + s_{\text{m}}^{\nu} + s_{\text{n}}^{\nu} + \dots) \mathcal{L}_{(\nu)}(\dots s_{\text{p}}^{\mu} + s_{\text{q}}^{\mu} + s_{\text{r}}^{\mu} + \dots)] \quad (3.16)$$

where s_{ℓ}^{ω} , s_{m}^{ω} etc., are the areas (in units of S) of rings ℓ , m , etc.,

contained in circuit ω . Finally, therefore, by expanding equation (3.16) and collecting together the coefficients of the terms s_i , representing the area of each ring in the polycyclic molecule, we may cast the result:

$$E^{(2)} = -\beta \left(\frac{2\pi e}{h} \right)^2 S^2 B_o^2 \left\{ \sum_i J_i s_i \right\} \quad (3.17)$$

where the J_i - terms (proportional — see below — to the "ring-current" intensity in ring i of the molecule) are precisely the J_i of McWeeny's equation (6.1) in ref. 132. Now, for a molecular dipole, $\mu = \mu(B_o)$, arising from the field-proportional induced-currents, the second-order energy is

$$E^{(2)} = \frac{-\chi B_o^2}{2\mu_o} = -\frac{1}{2} \mu(B_o) \cdot B_o \quad (3.18)$$

in which χ is the diamagnetic susceptibility. $|\mu|$ therefore follows from equation (3.17), and, comparison with the classical form²⁰

$$|\mu| = \sum_r I_r S s_r, \quad (3.19)$$

(where I_r is the absolute "ring-current" intensity in ring r) then permits an identification of the following expression for the "ring-current" intensity in ring r :

$$I_r = 8\pi^2 \beta \left(\frac{e}{h} \right)^2 S B_o J_r \quad (3.20)$$

which is equivalent to the formula obtained by Pople¹³¹ making use, in the final stages of his calculation, of a test dipole, but basically using the 'London' gauge-factors defined by equations (3.1) and (3.2), i.e. not including the dipole effect on the LCAO basis-functions.

We note, therefore, that since the J_i -terms of equation (3.17) are exactly those of McWeeny's equation (6.1) in ref. 132, we have shown that if, in this approach, we employ the gauge factor defined by equation (3.3), such a procedure does not affect the calculated "ring-current" intensities — i.e. the same induced-current distribution results as when the gauge factor defined in equation (3.2) is used. What we have done here is essentially to justify the observation²⁰ that the "ring-current" intensities derived by the McWeeny method¹³² (using gauge factors defined by equations (3.1) and (3.3)) are exactly those implicit in the London method³ (based on equations (3.1) and (3.2)) which can predict only the total magnetic-susceptibility of a conjugated, polycyclic molecule, and not that (formally) associated with each individual-ring. (This statement can be verified if, for example,²⁰ "ring currents" calculated^{132,82,114,116,140,141,155} by the method of McWeeny¹³² or Pople¹³¹ are used (via equation (3.19)) to estimate $\chi_{\text{molecule}}^{\pi \text{ London}} / \chi_{\text{benzene}}^{\pi \text{ London}}$ ratios for those molecules for which such ratios have been calculated by the London method.^{3b,147a,147b,151}

3.5 'Bond Currents' and the Secondary Field Due to the Induced-Current Distribution

We now have to investigate how this induced-current distribution affects the secondary magnetic-field at any point in space in the vicinity of the molecule, and, for this purpose, it is pedagogically convenient to reduce our formal concept of "ring currents" to one of 'bond currents'; for, as McWeeny¹³² and Salem²⁰ have observed, and Chapter VI develops in some detail, the induced-current distribution in the conjugated molecule may formally

be considered as a sum of individual 'bond-currents' to be associated with each bond, $i-j$, in the molecule. The J_r -terms of equations (3.17) and (3.20) (associated with each ring, r , of the molecule, and proportional, via equation (3.20), to what we are calling the "ring-current" intensity in that ring) may be broken down into contributions from the individual bonds, $(i-j)$, so that (cf. equations (3.13) and (3.17)):

$$J_{ij}^{\text{bond}} = (P_{ij} + \beta \bar{\pi}(ij)(ij)) s_{ij} + \sum_{kl \neq ij} \beta \bar{\pi}(ij)(kl) s_{kl}. \quad (3.21)$$

It is important to note in passing that, in the simple McWeeny-'test-dipole' approach,¹³² which employs Hückel-type assumptions about neglect of non-neighbouring interactions, the 'bond current' (equation (3.21)) is, within the approximations of the theory (and within those of the London-type approach being adopted here), a formally definable, exactly calculable, quantity, and is entirely equivalent, without further approximation, to the concept of a "ring current". Recently, Amos and Roberts have discussed the idea of 'bond currents' arising from calculations using the current-density approach (§3.3) in an uncoupled-Hartree-Fock context.^{175a} In this case, the induced-current densities are calculated via equation (3.4), using an SCF wave-function, and conservation of such 'bond-current' densities is by no means obtained—Amos and Roberts calculate^{175a}, for the 'bond currents' in naphthalene, values of 1.11, 1.04 and 1.07 for the 1-2, 2-3 and 1-9 bonds, respectively (with, of course, zero intensity, by symmetry, for the current associated with the 9-10 bond). It has been stated^{175a} that this non-conservation of 'bond-current' densities is possibly due to the use of the Feenberg-Goldhammer 'geometric'-correction¹⁹⁵, by means of which a 'coupled' Hartree-Fock calculation is simulated from an 'uncoupled' one — although recent work by Coulson, Gomes and the present author¹⁶², and by Atkins and Gomes²⁶⁸, has shown that entities of this sort are not strictly bound to obey any Kirchhoff-type of conservation

law. In the Hückel-McWeeny formulation, however, since non-neighbouring interactions are neglected in the wave function right from the start, and no subsequent 'corrections' are required, no further approximation results if the concept of a 'bond' is introduced, with the result that 'conservation of current' (in the 'Kirchhoff-network' sense) is in fact maintained. Thus, in naphthalene, the J_i ("ring-current") terms of equations (3.17) and (3.20) are 1.093, relative to benzene¹³² for both rings, and J_{12}^{bond} , J_{23}^{bond} and J_{19}^{bond} , calculated from equation (3.21), are all exactly 1.093. Hence, discussion of 'bond currents' in the Hückel-McWeeny context is entirely consistent with the approximations inherent in the type of LCAO wave-function employed.

Now, in the current-density approach (§3.3), having calculated, quantum mechanically, the induced π -electron current-densities, $J_{oj}(\underline{r}_j)$, in the molecule, we estimate the secondary field by means of a classical expression of the form of equation (3.5); by analogy*, therefore, in the present calculation, having formally reduced our quantum-mechanically calculated induced-current distribution to a set of 'bond currents', J_{ij}^{bond} , we could, following the suggestion of McWeeny¹³² and Longuet-Higgins and Salem^{20,127} further consider

* The reader should understand, however, that the resemblance between the current-density method (§3.3) and the present procedure is only superficial; there is merely a similarity of methodology; for, in the current-density approach, $J_{oj}(\underline{r}_j)$ in equation (3.5) is a quantum-mechanical current-density; but, in equation (3.25), J_{ij}^{bond} , though of the magnitude of the entirely quantum-mechanical 'bond-current' computed in equation (3.21), is, in fact, a classical 'line-current' in the way in which it contributes to the scalar magnitude of the total secondary-field in equation (3.25). The present procedure (being, essentially, that due to Longuet-Higgins and Salem^{127,20}) is, therefore, strictly a retrograde step away from the entirely quantum-mechanical McWeeny-approach¹³², and some apologia are needed for using it; in fact, this approach has been adopted in order, as will be seen (§3.6), to show that its numerical approximations tend, at points distant from ring centres, to those implicit in McWeeny's procedure of inserting a dipole into the gauge factor, as in equation (3.3).

these quantum-mechanical 'bond-currents' as classical 'line-currents', and then estimate the secondary field due to them by means of a classical formalism such as the Biot-Savart Law, as discussed in §1.3(v)(d). It should be emphasised, however, that by making this latter change from quantum-mechanical 'bond-currents' to classical 'line-currents', we have transgressed the realms of what, until now, has been an entirely quantum-mechanical theory, to a semi-classical one. The Biot-Savart Law states that the field at the origin due to an element ds related to the origin by $\underline{r}$ and bearing unit current, is¹²⁹:

$$\underline{B}' = \frac{\mu_0}{4\pi} \int \frac{ds \times \underline{r}}{r^3} \tag{3.22}$$

which, for a 'wire' (bond) of finite length bearing a current $I_{ij}^{bond} = TJ_{ij}^{bond}$ (the constant T being the coefficient of J_r on the right-hand-side of equation (3.20)) reduces (with symbols as defined in Figure 3.1 and with Q written for $T \frac{\mu_0}{4\pi}$) to¹²⁸

$$B'_{ij} = QJ_{ij}^{bond} \cdot \frac{1}{R_{ij}} (\cos \alpha_{ij} + \cos \gamma_{ij}), \tag{3.23}$$

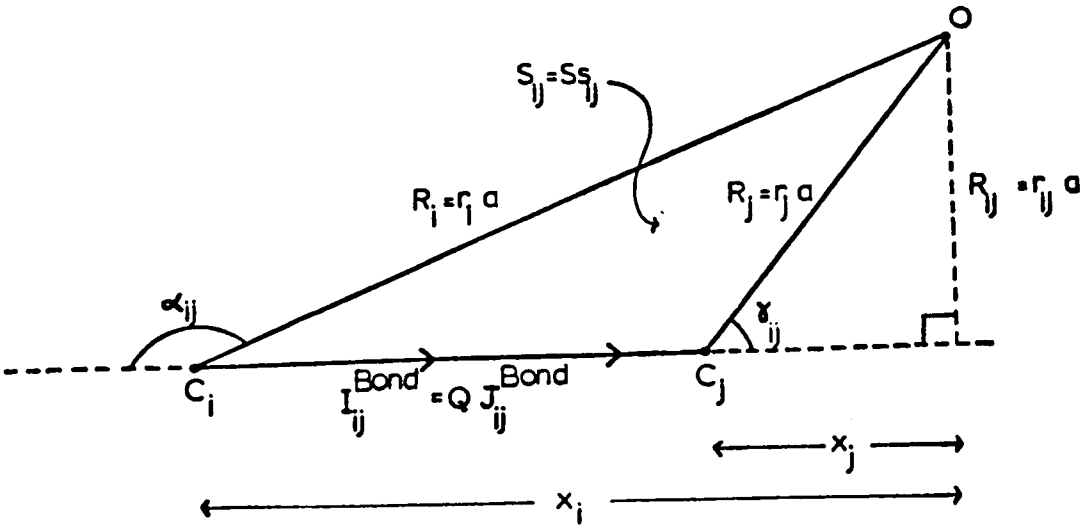


FIGURE 3.1

$$= \frac{QJ_{ij}^{bond}}{a} \cdot F_{ij}^{BS} \text{ (say),} \tag{3.24}$$

B'_{ij} being the magnitude of $\tilde{B}'_{ij}$, perpendicular to the plane, O_{ij} , of the molecule (for convenience we here consider O to be in the molecular plane, but this restriction is, of course, not necessary^{38b,111}; (see also §14(j))).

It should be observed that, contrary to initial appearances, there is, in fact, no discontinuity as $R_{ij} \rightarrow 0$ in equation (3.23) (as not infrequently happens in the calculations being described); because, as $R_{ij} \rightarrow 0$, $\alpha_{ij} \rightarrow \pi$, and $\gamma_{ij} \rightarrow 0$, it can be shown that B'_{ij} does tend correctly to zero, in the limit.

From equation (3.24) we can now write the total secondary-field at the origin, O , from all bonds, $i-j$, in the molecule, as

$$B' = \sum_{(ij)} \frac{Q}{a} \{J_{ij}^{\text{bond}} F_{ij}^{\text{BS}}\} \quad (3.25)$$

Comparison of equation (3.21) with McWeeny's equation (4.4) (of ref. 132) and equation (3.25) shows that the latter is entirely equivalent to McWeeny's equation, except that his factor $(S/a^2) s_{ij} k_{ij}$, where (Figure 3.1)

$$\begin{aligned} s_{ij} k_{ij} &= s_{ij} (1/r_i^3 + 1/r_j^3) \\ &= F_{ij}^{\text{McW}} \quad (\text{say}), \end{aligned} \quad (3.26)$$

is replaced by F_{ij}^{BS} , defined

$$F_{ij}^{\text{BS}} = \frac{1}{r_{ij}} (\cos \alpha_{ij} + \cos \gamma_{ij}). \quad (3.27)$$

Hence we see that use of the gauge factor defined in equation (3.3) (in conjunction with a quantum-mechanical 'bond-current', TJ_{ij}^{bond}) is equivalent to calculating the field at the origin due to a classical line-current, $I_{ij}^{\text{bond}} (=TJ_{ij}^{\text{bond}})$, in the bond $i-j$ via equation (3.25),

but with F_{ij}^{BS} (equation (3.27)) replaced by $(S/a^2) F_{ij}^{McW}$ (equation (3.26)).

In the "ring-current" jargon, we could say (after performing the unitary transformation amongst the basis orbitals¹³²) that the $(S/a^2) K^{McW}(\underline{r}_i)$ -terms* of McWeeny's equation (6.1) (of ref 132), in which $K^{McW}(\underline{r}_i)$ is defined

$$K^{McW}(\underline{r}_i) = \sum_{\substack{k \rightarrow l \\ \text{around} \\ \text{the } i\text{th ring}}} s_{kl} (1/r_k^3 + 1/r_l^3), \quad (3.28)$$

are now replaced by $K^{BS}(\underline{r}_i)$, defined

$$K^{BS}(\underline{r}_i) = \sum_{\substack{k \rightarrow l \\ \text{around ring } i}} 1/r_{kl} (\cos \alpha_{kl} + \cos \gamma_{kl}), \quad (3.29)$$

where the sums are taken in the anti-clockwise direction around ring i .

Finally**

$$B' = \frac{2\beta}{3} \left(\frac{2\pi e}{h} \right)^2 \frac{\mu_0 S}{4\pi a} B_0 \left\{ \sum_i J_i [-K^{BS}(\underline{r}_i)] \right\}, \quad (3.30)$$

(where a factor of $\frac{1}{3}$ has been added to take account of averaging the secondary field over all orientations of the molecule with respect to

*For consistency of notation, what McWeeny calls ' $K(\underline{r}_i)$ ' in ref. 132 we here denote ' $K^{McW}(\underline{r}_i)$ '.

** It should be pointed out that, in equations (3.23) - (3.30), the dimensions may, at first sight, look wrong, although, actually, with McWeeny's symbolism, they are correct; s_{ij} , k_{ij} , F_{ij}^{BS} and r_{ij} are, in fact, all dimensionless — as are the quantities J_r (equation (3.20)) and $J_{\text{bond } ij}$ (equation (3.21)).

the external magnetic-field^{111,140,175a*.})

The substitution of $(S/a^2)F_{ij}^{McW}$ (equation (3.26)) for F_{ij}^{BS} (equation (3.27)), and of $K^{BS}(\underline{r}_i)$ (equation (3.29)) by $(S/a^2)K^{McW}(\underline{r}_i)$ is evidently going to have the greatest consequence when points near the molecule are considered for, as McWeeny pointed out originally,¹³² this resolution of the total magnetic-effect into terms associated with the various rings (or, as here, bonds) is essentially formal; it will be accurate in giving the secondary field at large distances, where only the total moment matters, but will not necessarily be satisfactory near the molecule.

Our conclusions from this sub-section, therefore, are that:

(1) Those calculations which have used the original McWeeny-method to estimate relative "ring-current" intensities^{132,82,114,116,140,141,155} are unaffected by the insertion of a dipole contribution into the gauge factor (equation (3.3)), remain inviolate to this recent critique²¹⁹ and are, therefore, entirely as valid (or otherwise) as the results of the London³ and Pople¹³¹ approaches, which use the simpler gauge-factors defined by equations (3.1) and (3.2).

(2) Those calculations which have used the McWeeny method to estimate "ring-current" secondary-fields (and, hence, screening-constants)¹³² are, however, open to these considerations²¹⁹, in that F_{ij}^{BS} and $K^{BS}(\underline{r}_i)$ in the present treatment are replaced by $(S/a^2)F_{ij}^{McW}$ and $(S/a^2)K^{McW}(\underline{r}_i)$, respectively, as a result of the use of the gauge factor of equation (3.3), and quantum-mechanical 'bond-currents'. Therefore, the consequences of using the gauge factor defined in equation (3.2), and employing the 'line-current' formalism adopted here, instead of inserting a dipole contribution into the gauge factor (equation (3.3))

¹³⁰
* Haddon has independently used a 'Biot-Savart-Law' approach to study the proton chemical-shifts in annulenes. His method differs from the one described here in a number of important respects, notably in the use of what is termed the 'split-loop' ring-current model, and in the fact that individual "ring-current" intensities are not calculated, but are deduced from a statistical comparison with experimental chemical-shifts.

but retaining quantum-mechanical 'bond-currents', thus have to be assessed by investigating how different the quantities $(S/a^2)K^{\text{McW}}(\underline{r}_i)$ and $K^{\text{BS}}(\underline{r}_i)$ are for various points in space; such an empirical appraisal is made in the next sub-section.

3.6 Numerical Calculations

It seems likely that the differences just referred to will be greatest for points near a bond i - j , but they may not be so large for more-distant points from that bond; Salem²⁰ has investigated this in the case of naphthalene, but it is of interest here to revise the results of the original McWeeny-approach for a wide range of condensed, benzenoid molecules (sixteen in all) for which suitable experimental chemical-shift data are available^{60,174} and which have already been studied from the viewpoint of the original McWeeny-method^{170,171,140} and the semi-classical Waugh-Fessenden-Johnson-Bovey^{15,117,118} approach (Chapter II)* and will, therefore, afford comparison*; this we now do.

Table 3.1 shows all the $K^{\text{BS}}(\underline{r}_i)$ ('Biot-Savart') geometric-factors required for the calculations on the sixteen molecules studied (nomenclature and proton numbering as in Figure 2.1) together with the corresponding $(S/a^2)K^{\text{McW}}(\underline{r}_i)$ ('McWeeny') geometric-factors^{111,173} for comparison. The left-hand column gives the geometric relation between a particular proton, considered as origin, and the ring around which the summations of equations (3.28) and (3.29) are taken—e.g. 'Pentaphene 3' implies the instruction to take the origin, 0, (Figure 3.1) at proton 3 in pentaphene and then perform the summations (3.28) and (3.29) in an

* These data^{60,174} have also been used to test predictions of the 'test-dipole' method in both coupled^{176a} and uncoupled^{176b} Hartree-Fock SCF-contexts.

anti-clockwise direction around that ring in pentaphene, the centre of which is most distant from proton 3.^{111,173} As can be seen from the first row of Table 3.1, when the origin is set at a standard benzene-proton, and the summations (3.28) and (3.29) are performed around a standard benzene-ring, $(S/a^2)|K^{McW}(\underline{r}_i)|$ is greater than $|K^{BS}(\underline{r}_i)|$ by about 50%. However, going only to naphthalene, proton 1, we find that these two quantities already differ by an order-of-magnitude less (<3%) and, as can be seen by inspection of Table 3.1 (and as was anticipated above), the difference between $(S/a^2)K^{McW}(\underline{r}_i)$ and $K^{BS}(\underline{r}_i)$ very rapidly falls towards zero as the distance between the proton considered and the centre of the ring of interest increases until, for the most-distant points considered in Table 3.1, these two quantities become identical, to the number of decimal places computed.

More generally, we can say that $x_i, x_j \ll r_{ij}$ (see Figure 3.1, where, as always, the lengths x_i and x_j are measured in units of a , benzene carbon-carbon bond-length), and a binomial expansion of the expressions in equations (3.28) and (3.29) leads to:

$$K^{BS}(\underline{r}_\ell) = \sum_{\substack{\text{Bonds } i \rightarrow j \\ \text{around ring } \ell}} - \frac{1}{r_{ij}} \left\{ \frac{(x_i - x_j)}{r_{ij}} - \frac{1}{2} \frac{(x_i^3 - x_j^3)}{r_{ij}^3} + \dots \right\} \quad (3.31)$$

and

$$(S/a^2)K^{McW}(\underline{r}_\ell) = \sum_{\substack{\text{Bonds } i \rightarrow j \\ \text{around ring } \ell}} - \frac{1}{r_{ij}} \left\{ \frac{(x_i - x_j)}{r_{ij}} - \frac{3}{4} \frac{(x_i - x_j)(x_i^2 + x_j^2)}{r_{ij}^3} + \dots \right\} \quad (3.32)$$

We note, therefore, that, as anticipated, the two quantities are equal, to first order; as the second-order term vanishes, this explains the near-equality of most pairs of numbers in Table 3.1. The two expressions differ only in the third-order term, important for small values of r_{ij} (such as occur, for example, in the benzene, naphthalene-1 and, to a

lesser extent, naphthalene-2 geometric-factors), but not important for more-distant points from ring centres.

In calculating the J_i ("ring-current") factors required for the application of equation (3.30) (the expression for which is implied by equations (3.13)-(3.17)), the following explicit general-formulation is useful, for any particular set of 'circuits',^{132,111,141} constructed from any arbitrary 'open-chain',^{132,111,141} contained within the molecule*.

$$J_i = \sum_{(\mu)} \left[P_{(\mu)} n_{(\mu)} + \beta \pi_{(\mu)} n_{(\mu)}^2 \right] \mathcal{S}_{(\mu)} \mathcal{L}_{(\mu)}^i + \sum_{(\mu)} \sum_{\substack{(\nu) \\ (\mu < \nu)}} \beta \pi_{(\mu)(\nu)} n_{(\mu)} n_{(\nu)} \\ \times \left[\mathcal{S}_{(\mu)} \mathcal{L}_{(\nu)}^i + \mathcal{L}_{(\mu)}^i \mathcal{S}_{(\nu)} \right], \quad (3.33)$$

where: $\beta_{(\omega)}$ (the resonance integral for the ω th 'circuit-completing' bond) = $\beta n_{(\omega)}$ (but we here assume all $n_{(\omega)} = 1$), $\mathcal{S}_{(\omega)}$ is the area of the ω th circuit and $\mathcal{L}_{(\omega)}^i = 0, \pm 1$;

$\mathcal{L}_{(\omega)}^i = +1$ if, (a) the ω th circuit contains the ring i , and
if (b) the ω th circuit-completing bond¹³² is defined in the positive (anti-clockwise) sense around the circuit which it completes (the ω th circuit).

$\mathcal{L}_{(\omega)}^i = -1$ if (a) above applies and
if (b) the ω th circuit-completing bond is defined in the clockwise direction around the ω th circuit.

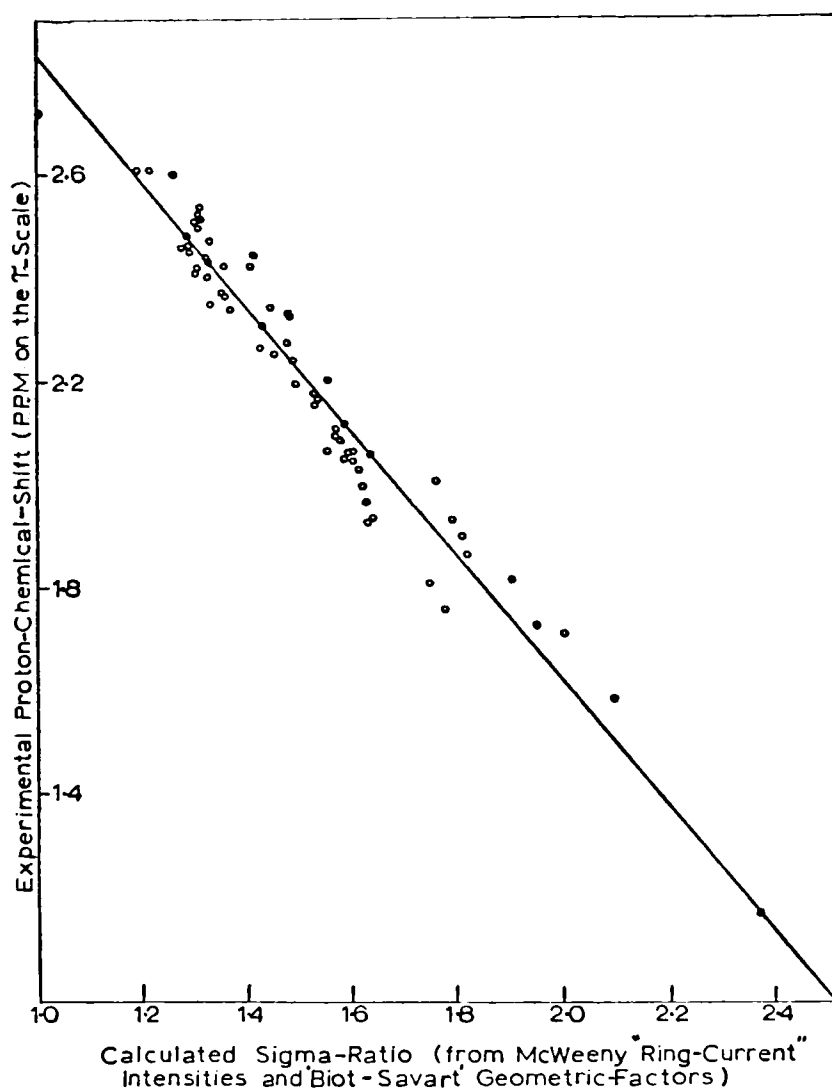
$\mathcal{L}_{(\omega)}^i = 0$ if the ω th circuit does not contain the ring i .

Hence, with the $K_{\tilde{r}_i}^{BS}$ -terms from equation (3.29), and J_i -terms

* A fuller discussion of 'circuits' and 'open-chains' will be taken up in Chapter VI, where the graph-theoretical aspects of "ring-current" calculations will be examined.

FIGURE 3.2

Experiment-vs.-Theory Regression-Line
 (Equation (3.34)) with (B'_r/B'_{benzene})-
 Ratios Calculated via Equations (3.30),
 (3.29) and (3.33)



via equation (3.33) (or, in appropriate cases, from the Literature;^{32,114,116 141,155}) equation (3.30) can now be applied to all the sterically-non-hindered

protons (66 in all) in the sixteen molecules studied; following previous treatments,^{132,140,141,169,170-172,176,192} we calculate the quantity B'/B'_{benzene} (where B'_{benzene} is obtained from equation (3.30), in which $J_i = J_{\text{benzene}}$ ($=1/9$), and $-K^{\text{BS}}(\tilde{r}_{\text{benzene}}) = 0.6583$ (Table 3.1)) and then regress this quantity against the corresponding experimental proton-chemical-shifts^{60,174} (τ values). The resulting regression-line is shown in Figure 3.2, and the details are given in Table 3.2, where 'sigma ratios' calculated^{140,170,171} by the original McWeeny-method¹³² are also included for comparison. Compound- and proton nomenclature are again as in Figure 2.1. The equation of this line is:

$$\tau_{\text{obs.}} = -1.21 (B'/B'_{\text{benzene}}) + 4.04 \quad (3.34)$$

(standard error in the slope: 0.032 ppm (2.6%); that in the intercept, 0.049 ppm, with a linear correlation-coefficient of -0.98, and total rms-deviation for all points of 0.061 ppm). It is seen that the correlation is marginally higher (0.98 as against 0.96) than when the original McWeeny-method¹³² was applied¹⁴⁰ to the same set of experimental data and the standard errors and the rms-deviation are, accordingly, slightly lower. The slope (-1.21 ppm) is what, on this parametrisation, must be interpreted as the "ring-current" contribution to the downfield shift of a benzene proton, and it should be noted that it is quite different from the value of -1.56 ppm previously obtained¹⁴⁰ via the unmodified McWeeny method¹³².

We note also that this value of -1.21 ppm is nearer to those (in the region of -1.0 ppm) resulting from various non-empirical calculations.^{242,175b} It is also different from that of another parametrisation recently found to be appropriate¹⁷⁶ for sigma-ratios calculated from uncoupled- and coupled

Hartree-Fock wave-functions, via the 'test-dipole' formalism,^{132,172}

Use of this present value of -1.21 ppm, together with $J_{\text{benzene}} = 1/9$, $K^{\text{BS}}(\tilde{r}_{\text{benzene}}) = -0.6583$, gives rise (via equation (3.30)) to an estimate of β , the standard carbon-carbon Hückel resonance-integral, of 42.8^* Kcal mol⁻¹ (an increase of some 20% on the previous estimate¹⁴⁰).

It is of interest to consider the differences between the B'/B'_{benzene} ('sigma') ratios¹⁴⁰ calculated on the basis of the original McWeeny-method¹³² (Table 3.2, column 1) and those evaluated by the present procedure (Table 3.2, column 2). Because the $K^{\text{BS}}(\tilde{r}_i)$ -factor for a benzene proton is smaller (numerically) than the corresponding $(S/a^2)K^{\text{McW}}(\tilde{r}_i)$ ('McWeeny') geometric-factor (Table 3.1) and yet these quantities tend to the same value at larger distances (see previous discussion), and also because such a $K^{\text{BS}}(\tilde{r}_{\text{benzene}})$ -term is used in the denominator (and, in general, amongst other smaller terms which are almost unchanged from the 'McWeeny' ones, in the numerator) of every B'/B'_{benzene} ('sigma') ratio, it follows that sigma ratios evaluated by the present procedure will be either equal to (in the sole case of benzene itself) or — in all other cases— greater than, the corresponding ratio calculated from the original McWeeny-method (see Table 3.2, columns 1 and 2, for confirmation of this). We see, therefore, that even though the sigma ratios obtained here are quite different from those obtained previously,^{170,171,140} these differences can be reconciled simply by using a different empirical-parametrisation (equation (3.34)) from the one (equation (2) of ref. 140) which was found to be appropriate¹⁴⁰ for sigma ratios calculated on the basis of the original, unmodified McWeeny-theory, and the resulting correlation is equally as good (Figure 3.2 and Table 3.2). This observation should, therefore, be heeded as a warning against too-literal an interpretation of such parametrisations (see §3.7).

* Ca. 180 K J mol⁻¹

3.7 Conclusions

It is concluded, therefore, that if we use the present approach in an attempt to preserve the simple elegance of the original McWeeny-formalism¹³², whilst discarding the recently-criticised²¹⁹ 'test-dipole' contribution to the vector potential in the gauge factor (equation (3.3)), we are led (without making specific reference either to a 'test dipole' or to the current-density operator), to an empirical theory of proton chemical-shifts in conjugated molecules, the predictions of which correlate as well with experiment as do those of the original McWeeny-approach¹³² — but the method does require a different empirical-parametrisation. Unfortunately, therefore, it does seem that attempts, by this sort of procedure, to attribute absolute empirical-values to those parameters which are apparently physically meaningful (e.g. "the ring-current contribution to the chemical shift of a benzene proton") should be treated with more caution than the present author, for one, previously^{140,111} thought necessary. Furthermore, because the approximations of these "ring-current" theories are least valid for the estimation of secondary fields at points near a benzenoid ring, those parametrisations based on a calibration with experimental data for points close to conjugated rings (e.g. equation (3.34) here, or equation (2) of ref. 140) will not necessarily be appropriate for deriving absolute shieldings from the relative shifts predicted, by the theory, at more-distant points (where, paradoxically, the actual approximations of the theory do, in fact, become more tenable than they are for points in close proximity to ring centres); for, those features of such empirical parametrisations which are devised especially to compensate for the particularly gross approximations of the theory when concerned with points near aromatic rings, will (if such parametrisations are injudiciously applied), persist, quite out of context, in the estimation of secondary fields at the more-distant points. This reservation should be borne in mind when interpreting calculations (or

numerical tables, such as those made available by the present author and Haigh¹³⁸) which are based on this type of parametrisation. Such considerations apply rather more subtly to the long-distance predictions of the semi-classical "ring-current" theories,^{15,117} because of the different way in which these theories are empirically parametrised (for discussion on this see Chapter II and ref. 138).

Included by implication in the 'approximations' referred to above, though not specifically mentioned so far in this chapter, are the so-called 'London approximations',^{3,20,38b,111,162} normally made in these calculations (see §1.4(i)(e)); (these are, essentially, that $\underline{r}$ in equation (3.1) can be replaced by $\frac{1}{2}(\underline{R}_i + \underline{R}_j)$ in the vicinity of the bond $i-j$). Doubt is increasingly being cast on this step, and it is now generally agreed that, at least in the context of less-empirical schemes, the London Approximation is inadequate^{38b, 189, 177}. Discussion of this approximation is, strictly, outside the scope of the present chapter, in which we have been concerned solely with the different approximations which the choice of various gauge-factors introduces into the London-McWeeny formalism. However, it is relevant to point out, by analogy with our arguments in the previous Section, that the London approximation is again going to be most severe for the contribution of carbon-carbon bonds $i-j$ and $j-k$ to the secondary field of a proton bonded to carbon-atom j , as Roberts has recently investigated in detail¹⁷⁷; furthermore, this geometric situation occurs in benzene and, indeed, for all the protons in condensed, benzenoid hydrocarbons (§3.6), and does, of course, give rise to the most-important contribution to the shielding constant of each proton; because of this, Amos and Roberts^{175,189,177} and the present author and Haigh^{38b} have concluded that errors (arising particularly in the 'bonded ring'^{38b}) due to the London approximation are almost entirely absorbed by the particular empirical-parametrisation adopted.

Hence, by analogy with these considerations concerning the London approximations (and bearing in mind the discussion of §3.6), we must conclude that, in a semi-empirical scheme such as is adopted here and in ref 140 (as opposed to a more-proper ab-initio approach), any additional illegitimacy²¹⁹ involved in the procedure of including a dipole contribution to the vector potential appearing in the gauge factor¹³² is evidently quite simply compensated for, numerically, by an appropriate empirical-parametrisation. And, indeed, when all these various approximations are taken into account, we are apparently led to confirm, and even extend, the somewhat unwelcome conclusion of Amos and Roberts^{175,177,189} and of the present author and Haigh^{38b} that the very good account which the simple MO-theory of π -electron "ring-currents"^{132,169,172,176,192} (and the present procedure) has given^{140, 170-172,176} of the observed chemical-shifts^{60,174} in conjugated molecules, may well be due to fortuitous cancellations, and compensations of errors and approximations, arising from the common practice of (1) taking a ratio of all calculated screening-constants to the screening constant evaluated for a standard benzene-proton, and then (2) of regressing these calculated ratios against experimental proton-chemical-shifts.

Table 3.1 Geometric Factors Required for the Calculations.

Geometric situation	Geometric factor	
	'McWeeny'* $\frac{S}{a} K^{McW}(\tilde{r}_i)$	'Biot-Savart'† $K^{BS}(\tilde{r}_i)$
Benzene (I)	-1.0436	-0.6583§
Naphthalene 1	-0.2052	-0.2002
(II) 2	-0.0740	-0.0726
Anthracene 1	-0.0486	-0.0469
(III) 2	-0.0206	-0.0205
Phenanthrene 1 (or 3)	-0.0375	-0.0375
(IV) 2	-0.0253	-0.0249
1,2 Benzanthrane (VIII)		
2' (5)	-0.0169	-0.0168
3' (6)	-0.0105	-0.0105
4' (7)	-0.0130	-0.0130
8	-0.0333	-0.0335
Pentaphene 1	-0.0178	-0.0177
(XI) 2 (4)	-0.0076	-0.0075,
3	-0.0056	-0.0056
1,2;7,8 Dibenzanthracene		
(XV) 2'	-0.0163	-0.0162
3' (4')	-0.0085	-0.0085

* From refs. 111 and 173

† From equation (3.29)

§ In ref 20, Salem obtained a slightly different value for this quantity for the case of benzene; however, the value given here has been carefully checked, both by hand-calculation and by computer.

Table 3.2 Calculated and Observed Chemical-Shifts

Compound and Proton	(B'/B' _{benzene}) ratio		τ -Value τ		$\tau_{\text{obs.}} - \tau_{\text{calc.}}$
	Unmodified McWeeny	Present Method	Observed (refs.60, 174)	Calculated†	
Benzene (I)	1.000	1.000	2.730	2.830	-0.10
Naphthalene 1 (II)	1.308	1.425*	2.270	2.315	-0.04
2	1.170	1.214*	2.620	2.570	0.05
Anthracene 1 (III)	1.387	1.552	2.070	2.161	-0.09
2	1.197	1.260	2.610	2.515	0.10
9	1.707	1.940	1.640	1.691	-0.05
Phenanthrene 1 (IV)	1.365	1.494	2.200	2.231	-0.03
2	1.230	1.283	2.490	2.487	0.00
3	1.243	1.305	2.430	2.460	-0.03
9	1.278	1.445	2.350	2.290	0.06
Chrysene 2 (V)	1.411	1.601	2.070	2.101	-0.03
3	1.420	1.567	2.100	2.143	-0.04
4	1.266	1.328	2.480	2.432	0.05
5	1.281	1.353	2.380	2.402	-0.02
Triphenylene 2 (VI)	1.231	1.299	2.420	2.467	-0.05
Pyrene 1 (VII)	1.388	1.621	2.000	2.077	-0.08
3	1.635	1.804	1.900	1.855	0.04
4	1.498	1.592	2.070	2.112	-0.04
1,2 Benzanthracene (VIII)					
2'	1.249	1.322	2.410	2.440	-0.03
3'	1.227	1.287	2.475	2.482	-0.01
4'	1.357	1.488	2.245	2.238	0.01
3	1.223	1.408	2.450	2.335	0.11
4	1.273	1.481	2.280	2.247	0.03
5	1.429	1.598	2.050	2.105	-0.06

Table 3.2 (continued)

Compound and Proton	(B/B' _{benzene}) ratio		τ-Value ¶		τ _{obs.} — τ _{calc.}
	Unmodified McWeeny	Present Method	Observed (refs.60, 174)	Calculated†	
6	1.238	1.305	2.535	2.460	0.07
7	1.241	1.309	2.530	2.455	0.07
8	1.446	1.626	1.970	2.071	-0.10
10	1.707	1.946	1.725	1.683	0.04
1,2 Benzopyrene 2' (IX)	1.248	1.332	2.355	2.427	-0.07
4	1.482	1.590	2.070	2.115	-0.04
5	1.608	1.785	1.935	1.878	0.06
6	1.405	1.635	2.060	2.060	0.00
3,4 Benzopyrene 1 (X)	1.527	1.774	1.760	1.892	-0.13
2'	1.362	1.454	2.260	2.280	-0.02
3'	1.346	1.429	2.315	2.310	0.01
4'	1.550	1.743	1.810	1.929	-0.12
5	1.804	2.093	1.585	1.505	0.08
6	1.315	1.575	2.090	2.133	-0.04
7	1.284	1.529	2.160	2.189	-0.03
8	1.592	1.761	2.010	1.908	0.10
9	1.469	1.569	2.115	2.140	-0.03
10	1.627	1.815	1.865	1.842	0.02
Pentaphene 1 (XI)	1.447	1.632	1.930	2.064	-0.13
2	1.236	1.307	2.505	2.458	0.05
3	1.231	1.299	2.520	2.467	0.05
4	1.416	1.584	2.055	2.122	-0.07
5	1.660	1.898	1.820	1.742	0.08
6	1.187	1.407	2.425	2.337	0.09
Perylene 2 (XII)	1.110§	1.189	2.620	2.601	0.02
3	1.220§	1.358	2.430	2.396	0.03

(Footnotes on pp. 142/143)

/Continued

Table 3.2 (continued)

Compound and Proton	(B'/B' _{benzene})ratio		τ -Value [†]		$\tau_{\text{obs.}} - \tau_{\text{calc.}}$
	Unmodified McWeeny	Present Method	Observed (refs.60, 174)	Calculated†	
1,2;3,4 Dibenzanthracene (XIII)					
2'	1.214	1.290	2.460	2.478	-0.02
3'	1.205	1.277	2.470	2.494	-0.02
7	1.243	1.312	2.545	2.452	0.09
8	1.440	1.617	2.035	2.082	-0.05
1,2;5,6 Dibenzanthracene (XIV)					
2'	1.277	1.355	2.375	2.400	-0.02
3'	1.254	1.318	2.450	2.444	0.01
4'	1.392	1.532	2.180	2.185	-0.01
3	1.291	1.484	2.330	2.243	0.09
4	1.358	1.586	2.120	2.120	0.00
1,2;7,8 Dibenzanthracene (XV)					
2'	1.286	1.370	2.345	2.381	-0.04
3'	1.257	1.323	2.440	2.438	0.00
4'	1.393	1.534	2.170	2.183	-0.01
3	1.290	1.481	2.340	2.247	0.09
4	1.341	1.558	2.205	2.154	0.05
10	1.743	1.994	1.715	1.625	0.09
Coronene (XVI)	2.041	2.363	1.180	1.178	0.00

[†] From equation (3.34)

* In ref.20, Salem calculated slightly different sigma-ratios for naphthalene, by the present method; however, the values quoted here have been carefully checked, both by hand, and by computer.

§ In the footnote on p.753 of ref.140 discussion was included on a decision between Memory's values^{116a} for the "ring-current" intensities in perylene, and those of Jonathan et al.¹²⁰; those of Memory were favoured but, inadvertently, the "ring currents" of Jonathan et al. were, after all, used to compute the sigma ratios quoted for perylene in ref. 140. The correct values are quoted here: a 're-run' of the regression line discussed in ref. 140 with the correct sigma-ratios reported here (column 1) did not, however, change the slope and intercept of the 'best-fit' line, to the number of decimal places quoted in ref. 140.

Table 3.2 (continued)

- || As a result of a typographical error, the McWeeny sigma-ratio for 1,2;5,6 dibenzanthracene, Proton 3', was wrongly given as 1.245 in ref. 140 instead of (as here) 1.254.
- ¶ Modern authors seem increasingly to prefer the ' δ '-scale to the ' τ '-scale when discussing proton chemical-shifts; the present author, however, feels that there is a good case for retaining the τ -scale and it is, accordingly, used in this chapter. Any reader who disagrees with this policy is strongly referred to the closely reasoned arguments of Raynes²⁸²

CHAPTER IV

ON THE ALLEGED CORRELATIONS BETWEEN SIMPLE LCAO-MO REACTIVITY-INDICES AND PROTON CHEMICAL-SHIFTS IN PLANAR, CONDENSED, BENZENOID HYDROCARBONS

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CHAPTER IV

ON THE ALLEGED CORRELATIONS BETWEEN SIMPLE LCAO-MO
 REACTIVITY-INDICES AND PROTON CHEMICAL-SHIFTS IN PLANAR,
 CONDENSED, BENZENOID HYDROCARBONS*

4.1 Summary and Scope of the Chapter

In this Chapter we shall reassess Kuthan's²⁸³ proposed correlations between proton chemical-shifts in conjugated hydrocarbons and the various LCAO-MO 'reactivity-indices' at the corresponding carbon-atoms to which the peripheral protons are bonded. These alleged correlations will be reconsidered in the light of more-recently acquired experimental data for the case of planar, alternant, condensed, benzenoid hydrocarbons^{60,174}. A correlation coefficient of 0.73 is obtained, statistically 'significant' at less than $\frac{1}{2}\%$ level. Nevertheless, there are several unsatisfactory features of such proposed correlations (which will be discussed) and, in the final analysis, no causative relation is expected between proton chemical-shifts and reactivity indices in these molecules. Furthermore (as we have already seen in Chapters II and III), the relative chemical-shifts of the sterically unhindered protons in planar, alternant, benzenoid hydrocarbons may nicely be accounted for empirically by the "ring-current" effect alone, without the need to postulate a dependence of the proton chemical-shifts on reactivity indices, which is in any case considered to be unlikely on physical grounds. After publication^{*} of these results, this point is now conceded by Kuthan²⁸⁴.

* The contents of this Chapter have been published; the full reference is: R.B. MALLION, "On the Alleged Correlations Between Simple LCAO-MO Reactivity-Indices and Proton Chemical-Shifts in Planar, Condensed, Benzenoid Hydrocarbons", Organic Magn. Resonance, 1973, Vol. 5, pp.91-94.

4.2 Background to the Investigation

From Literature data concerning a number of planar and non-planar polycyclic, condensed, benzenoid hydrocarbons, Kuthan²⁸³ has suggested that correlations exist between the proton chemical-shifts in these molecules and various 'reactivity-indices' at the corresponding carbon-atoms to which the peripheral protons are bonded; these proposed correlations, together with extensions to non-alternant and heterocyclic molecules,^{285,286} have been used, for example, to examine the carcinogenic properties of the polycyclic unsaturated-hydrocarbons and their heterocyclic analogues²⁸⁷. Bartle and Jones have since extended these investigations to include other conjugated-hydrocarbons — planar and non-planar, alternant and non-alternant, substituted and unsubstituted — for which Literature chemical-shift data were then available, and they have concluded that statistically significant correlations do exist, but that these are 'fortuitous', those proton shifts deviating most from the regression lines involved being adequately explained by the so-called "ring-current" effects.²⁸⁸

Both these investigations, however, used chemical-shift data of varying accuracy — although these two groups of workers did make the important distinction between planar benzenoid-hydrocarbons (defined,^{140,38} in Martin's terminology,²⁴¹ as being those hydrocarbons containing no overcrowding more severe than is provided by H α 3-, H γ 3- or H γ 3,3 - interactions) and hydrocarbons such as 3,4 benzophenanthrene, which are clearly non-planar.^{38,142,289-291} Molecules with only H α 3- or H γ 3- interactions are expected to be planar, from strain-energy-minimisation calculations,¹⁴³ whilst those involving²⁴¹ H α 4-, H α 5- and higher interactions are non-planar^{38,142,289-291}. In this Chapter, therefore, we reassess these correlations: (a) confining our attention only to planar, alternant, unsubstituted benzenoid-hydrocarbons, and (b) using the same recently-acquired experimental chemical-shift data^{60,174} to which appeal was made in Chapters II and III. In these new data, all shifts have been measured from full, second-order, iterative analyses of

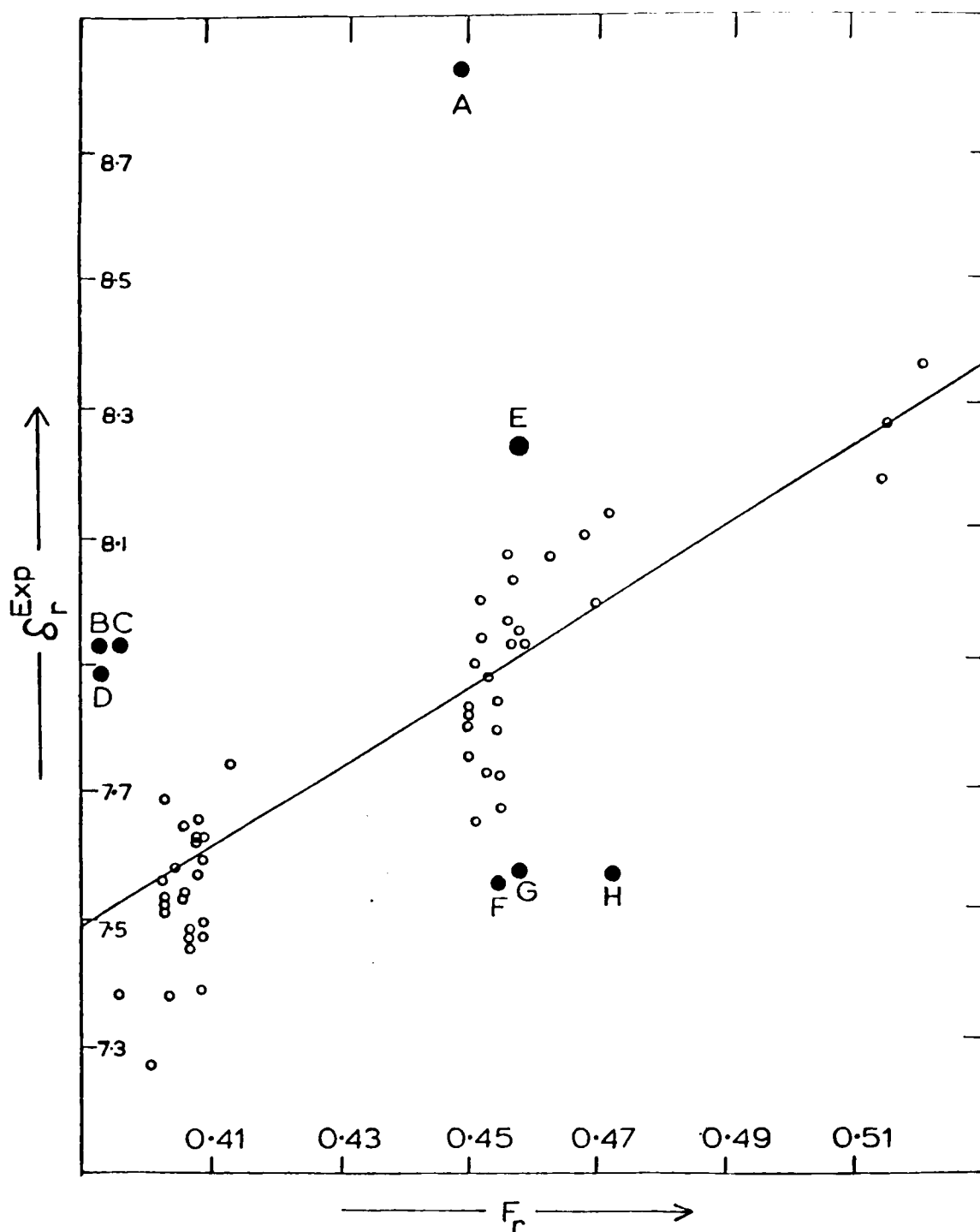
high-field (up to 220 MHz) spectra taken at (or near) 'infinite dilution' in a single solvent (CCl_4) chosen for its reasonably isotropic nature; the importance of concentration- and solvent effects on the proton chemical-shifts in benzenoid hydrocarbons has been stressed elsewhere^{38a,60,174,111,63}

Alternant and unsubstituted hydrocarbons are chosen because, on the simplest approximations, the charge density at each of their constituent carbon-atoms is unity¹⁰ — and there is evidence,^{292,293} on physical grounds, of a contribution to relative proton-chemical-shifts arising directly from net charges on the carbon atoms to which the protons are attached in non-alternant and substituted, conjugated hydrocarbons (see Part III of this Thesis). By choosing unsubstituted, alternant¹⁹⁷ molecules, we therefore eliminate, at this level of approximation, variation in charge density* as a potential contributor to the relative proton-chemical-shifts in the molecules under study. Planar molecules are chosen because of the additional complications (discussed in detail in refs. 38a and b) which arise when non-planarity is taken into account.

In all, 66 sterically non-hindered protons (i.e. 'non-angular' protons, in Kuthan's nomenclature^{283b}) are considered in the 16 different molecules for which chemical-shift data are available from refs. 60 and 174. For the purpose of attempted correlation with these, the 'free-valence' index²⁹⁴⁻²⁹⁶ is taken as being representative of the many LCAO-MO reactivity-indices (all of which have been shown to be related, both to each other,^{283b,288, 297} and to experimental reactivities^{288,298}).

* Charge density is itself often considered as a 'reactivity index', though, like 'free valence', 'atom-atom polarisability' etc., it is, in the context of the simple HMO-scheme, a purely topological quantity, (See also Chapter V) once the Aufbau Principle is accepted; (See a very recent article by Rouvray and the present author for a detailed discussion of this³⁰³).

FIGURE 4.1



Attempted Correlation Between Experimentally Observed Proton-Chemical-Shifts (the Ordinate) and the Free-Valence Index (the Abscissa) at the Corresponding Adjacent Carbon-Atom to Which the r th Resonating-Proton is Bonded.

The eight points depicted by full circles (and lettered A to H) represent sets of data which deviate from the "best-fit" line (equation (4.1)) by more than 0.30 ppm.

Key: (A) Coronene (Molecule (1) of Figure 4.2); (B) Pyrene(2), proton 4; (C) 1,2 Benzopyrene (3), proton 4; (D) 3,4 Benzopyrene (4), proton 9; (E) 3,4 Benzopyrene (4), proton 1; (F) 1,2 Benz-anthracene (5), proton 3; (G) Pentaphene (6), proton 6; (H) Perylene (7), proton 3.

4.3 Regression Correlations

Figure 4.1 shows a plot of δ_r^{Exp} vs. F_r for the 66 non-hindered protons studied; the 'best-fit' line through these points is

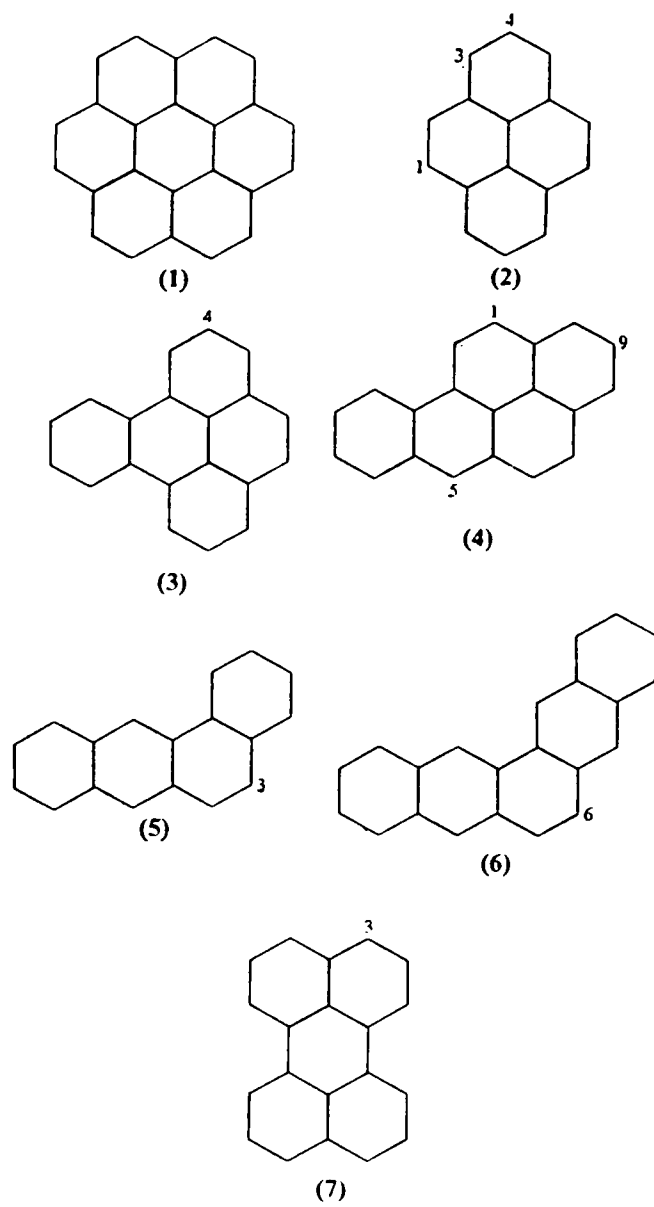
$$\delta_r^{\text{Exp}} = 6.25F_r + 5.05 \quad (4.1a)$$

$$\text{(or, } \tau_r^{\text{Exp}} = -6.25F_r + 4.95 \quad (4.1b))$$

with a standard error in the slope of 0.74 (11.8%) and a total RMS-deviation for all the points included of 0.20 ppm. The correlation coefficient, however, is only 0.73 — larger than that (0.63) obtained for a set of similar protons by Bartle and Jones,²⁸⁸ but much smaller than the value of 0.97 reported by Kuthan.^{283b} That the correlation coefficient of 0.73 reported here is indicative of a very poor linear relation between δ_r^{Exp} and F_r is confirmed by even a casual inspection of Figure 4.1, where deviations of up to about 1.00 ppm above the line (in the case of coronene, molecule (1) of Figure 4.2) and about 0.35 ppm below the line (1,2 benzanthracene (5) proton 3) are evident. The shifts of eight of the protons considered deviate from the line by more than 0.3 ppm and the data points representing these protons are lettered A to H in Figure 4.1 (for key, see the legend to this Figure). Almost a quarter of the points deviate from the line by 0.20 ppm or more; when the same experimental data as are considered here were correlated with relative shieldings predicted from simple "ring-current" theory (Chapters II and III and ref. 140), 0.20 ppm was the maximum discrepancy encountered — and even then only two protons out of the 66 exhibited such a deviation from the correlation line. More-detailed information on the deviations from the regression line (4.1) are given in Table 4.1, to be found at the end of this Chapter.

Bartle and Jones²⁸⁸ have concluded that the large deviations from the 'fortuitous' correlations, such as equation (4.1), are displayed by protons

FIGURE 4.2



Nomenclature of Protons Specifically Mentioned in
the Text (§ 4.3)

experiencing an unusually large chemical-shift due to the π -electron "ring-currents" in these molecules; coronene (1) and the pyrene (2) series [1,2- and 3,4 benzopyrenes, (3 and 4)] are described²⁸⁸ as 'compact, plate-like hydrocarbons' in which "ring-current" deshielding-contributions are expected to be of greater importance than in more 'open-chain' compounds. Thus, it is pointed out²⁸⁸ that the coronene proton (1) and protons 4 in pyrene (2) and in 1,2 benzopyrene (3) (Figure 4.2) are grossly anomalous. If we take the suggestion that there is a fortuitous δ_r^{Exp} vs. F_r correlation — partly masked in extreme cases, however, by "ring-current" effects acting simultaneously and independently — we are led to ask why, for example, protons 1 and 3 in pyrene (deviations of 0.12ppm) do not deviate more markedly from the line; these protons are in closer proximity to "ring-current" centres in this molecule than is proton 4. Similarly, in 1,2 benzopyrene (3), proton 4 is the only 'anomalous' proton (deviation: 0.41 ppm). Even more perplexing, if this hypothesis is maintained, is the fact that in 3,4 benzopyrene (4), only protons 1 and 9 deviate from the line by more than 0.3 ppm; however, the data for proton 5, which, being in the centre of the molecule, experiences the largest "ring-current" deshielding of any proton in the molecule, lie nicely on the line given by equation (4.1). The data for proton 3 in 1,2 benzanthracene (5), proton 6 in pentaphene (6) and proton 3 in perylene (7) all deviate greatly from equation (4.1) in the opposite direction to those for the above-mentioned protons in the pyrene series and in coronene; it might be argued, extending the Bartle-Jones reasoning,²⁸⁸ that these protons are all attached to, or are near, rings bearing exceptionally low "ring currents"^{140,116} and that these protons thus experience a correspondingly smaller "ring-current" deshielding — but again it is not clear why other protons in these molecules are not similarly 'anomalous'.

4.4 Conclusions

In view of the above considerations, instead of postulating that a 'fortuitous' correlation exists between proton chemical-shifts and simple LCAO-MO free-valence indices (and hence²⁹⁷ other reactivity indices) in alternant hydrocarbons, and further that these correlations are partially obscured in certain cases by "ring-current" effects, the present author would prefer to conclude more simply that, although the correlations such as (4.1) are certainly 'significant' in the narrow, statistical sense,* there is, for all practical purposes, no chemically useful relation between these quantities — whether these alleged correlations are said to be 'fortuitous',²⁸⁸ 'coincidental',³⁰⁰ 'causative',^{283b,301} or otherwise. The scatter of the points in Figure 4.1 and the low correlation - coefficient of 0.73 support this view. However, as was seen in Chapters II and III and in refs. 140 and 176, the relative experimental proton-chemical-shifts used in this discussion^{60,174} can be related to the corresponding secondary-magnetic-fields arising from what we are regarding as the π -electron "ring-currents" in these molecules, to give a correlation coefficient of better than 0.96 — whether these "ring-current" secondary fields are estimated quantum mechanically or semi-classically. Manifestly, therefore, the relative proton-chemical-shifts of the unhindered protons in planar, alternant, benzenoid hydrocarbons can be accounted for by the "ring-current" effect alone — without the need to postulate a dependence of the proton chemical-shifts

* The correlation coefficient of 0.73 obtained here for the 66 points shown in Figure 4.1 is 'statistically significant' at less than the $\frac{1}{2}\%$ level; this means²⁹⁹ that, statistically, there is less than a $\frac{1}{2}\%$ probability that a correlation as large as the 73% observed would arise by chance, in a sample of this size, randomly selected from a population of truly uncorrelated data. It should be noted, however, that the correlation coefficient gives information only about the quality of the correlation — it tells us nothing about whether the correlation under investigation arises in a causative manner as a result of some fundamental relation between the two quantities being correlated (as is erroneously argued for the present correlation by Kuthan and Krygowski³⁰¹, or in a fortuitous (*i.e.* 'coincidental') manner (as argued in this case by Bartle and Jones²⁸⁸).

on reactivity indices, which, in any case, seems physically somewhat unlikely.

This conclusion is reassuring for, in the final analysis, the chemical shift of a given peripheral-proton depends on the local magnetic-field at this proton and the quantum-mechanical formalism of the "ring-current" theory determines precisely how that local field shall be influenced by the contribution of a secondary magnetic-field due to what can be interpreted as the π -electron "ring-currents" (§1.4). On the other hand, in spite of the arguments recently advanced by Kuthan and Krygowski³⁰¹ (which have been examined critically and are, in fact, erroneous³⁰⁰), there appears to be no obvious mechanism whereby the value of a reactivity index at a given carbon-atom of an alternant hydrocarbon could have an influence in determining the local magnetic-field experienced by the proton attached to it*. In this regard, therefore, the present investigation supports the view of Bartle and Jones²⁸⁸ that one would have no reason to anticipate a causative relation between ^1H NMR chemical-shifts in alternant hydrocarbons and free-valencies — or indeed, between such chemical shifts and any of the other²⁹⁷ LCAO-MO reactivity indices. This point is now conceded by Kuthan²⁸⁴.

* It should be noted in passing that, from the work of Karplus and Pople,³⁰² the paramagnetic contribution to ^{13}C chemical-shifts is expected to depend on the 'free-valence' index; however, this term is explicitly zero if hydrogen atoms are involved^{263a}. Such correlations with F_r in the context of ^{13}C -shifts are, therefore, no reason for anticipating^{283b} any such $\delta_r^{\text{Exp}}:F_r$ relations when proton chemical-shifts are considered.

Table 4.1 Calculated and Observed Chemical-Shifts
of the Non-hindered Protons[†]

Compound and Proton	F _r [‡]	τ _{obs} [§]	τ _{calc} [*]	τ _{obs} - τ _{calc}
Benzene (I)	0.399	2.73	2.458	0.27
Naphthalene (II) 1	0.453	2.27	2.120	0.15
2	0.404	2.62	2.423	0.20
Anthracene (III) 1	0.459	2.07	2.079	-0.01
2	0.409	2.61	2.395	0.22
9	0.520	1.64	1.700	-0.06
Phenanthrene (IV) 1	0.450	2.20	2.137	0.06
2	0.403	2.49	2.434	0.06
3	0.408	2.43	2.402	0.03
9	0.452	2.35	2.128	0.22
Chrysene (V) 2	0.457	2.07	2.092	-0.02
3	0.451	2.10	2.128	-0.03
4	0.403	2.48	2.433	0.05
5	0.408	2.38	2.400	-0.02
Triphenylene (VI) 2	0.405	2.42	2.418	0.00
Pyrene (VII) 1	0.452	2.00	2.124	-0.12
3	0.468	1.90	2.023	-0.12
4	0.393	2.07	2.493	-0.42
1,2 Benzanthracene (VIII)				
2'	0.409	2.41	2.395	0.02
3'	0.403	2.475	2.430	0.04
4'	0.450	2.245	2.137	0.11
3	0.455	2.45	2.105	0.35
4	0.455	2.28	2.105	0.17
5	0.458	2.05	2.086	-0.04
6	0.407	2.535	2.404	0.13
7	0.408	2.53	2.397	0.13

(Footnotes on page 153)

/Continued

Table 4.1 (continued)

Compound and Proton		$F_r^\ddagger$	$\tau_{\text{obs}}^\S$	τ_{calc}^*	$\tau_{\text{obs}} - \tau_{\text{calc}}$
1,2 Benzopyrene (IX)	8	0.457	1.97	2.096	-0.13
	10	0.514	1.72 ₅	1.734	-0.01
	2'	0.405	2.35 ₅	2.415	-0.06
	4	0.396	2.07	2.477	-0.41
	5	0.463	1.93 ₅	2.053	-0.12
3,4 Benzopyrene (X)	6	0.452	2.06	2.127	-0.07
	1	0.458	1.76	2.085	-0.33
	2'	0.413	2.26	2.367	-0.11
	3'	0.403	2.31 ₅	2.432	-0.12
	4'	0.459	1.81	2.081	-0.27
	5	0.530	1.58 ₅	1.639	-0.05
	6	0.455	2.09	2.104	-0.01
	7	0.455	2.16	2.106	0.05
	8	0.470	2.01	2.012	0.00
	9	0.394	2.11 ₅	2.490	-0.38
Pentaphene (XI)	10	0.472	1.86 ₅	2.000	-0.14
	1	0.456	1.93	2.098	-0.17
	2	0.409	2.50 ₅	2.396	0.11
	3	0.407	2.52	2.404	0.12
	4	0.458	2.05 ₅	2.088	-0.03
	5	0.514	1.82	1.738	0.08
	6	0.458	2.42 ₅	2.086	0.34
Perylene (XII)	2	0.396	2.62	2.475	0.15
	3	0.473	2.43	1.996	0.43
1,2;3,4 Dibenzoanthracene (XIII)	2'	0.406	2.46	2.415	0.05
	3'	0.406	2.47	2.414	0.06

(Footnotes on page 153)

/Continued

Table 4.1. (continued)

Compound and Proton	$F_r^\ddagger$	$\tau_{\text{obs}}^\S$	τ_{calc}^*	$\tau_{\text{obs}} - \tau_{\text{calc}}$
7	0.407	2.54 ₅	2.405	0.14
8	0.456	2.03 ₅	2.099	-0.06
1,2;5,6 Dibenzanthracene (XIV)				
2'	0.409	2.37 ₅	2.395	-0.02
3'	0.403	2.45	2.432	0.02
4'	0.450	2.18	2.135	0.04
3	0.455	2.33	2.103	0.23
4	0.453	2.12	2.117	0.00
1,2;7,8 Dibenzanthracene (XV)				
2'	0.408	2.34 ₅	2.397	-0.05
3'	0.403	2.44	2.429	0.01
4'	0.450	2.17	2.137	0.03
3	0.454	2.34	2.112	0.23
4	0.454	2.20 ₅	2.110	0.10
10	0.510	1.71 ₅	1.765	-0.05
Coronene (XVI)	0.449	1.18	2.143	-0.96

† Compound nomenclature and proton numbering are as in Figure 2.1

‡ Taken from the tabulations of ref. 294.

§ Observed τ -values (all at infinite dilution, or very low concentration (<0.3 mole %) in CCl_4) from refs. 60 and 174.

* From equation (4.1b)

PART THREE

TOPOLOGICAL ASPECTS OF SIMPLE
"RING-CURRENT" CALCULATIONS AND
RATIONALISATION OF RELATIVE
"RING-CURRENT" SIZES

CHAPTER V

THE TERMINOLOGY AND METHODS OF GRAPH THEORY AND THE GRAPH-THEORETICAL ASPECTS OF HÜCKEL MOLECULAR-ORBITAL CALCULATIONS

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CHAPTER V

THE TERMINOLOGY AND METHODS OF GRAPH THEORY
AND THE GRAPH-THEORETICAL NATURE OF HÜCKEL MOLECULAR-ORBITAL CALCULATIONS

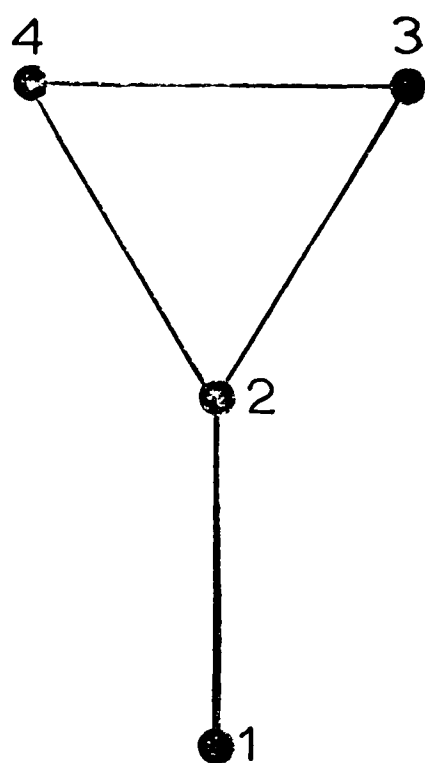
5.1 Introduction

In Part Three of this Thesis, which begins with the present chapter, we leave the empirical, predictive powers of simple theories of the "ring-current" effect and turn our attention to the more-abstract, mathematical basis which underlies them. The next three chapters will therefore be devoted to an investigation of the topological aspects of simple "ring-current" calculations and will exploit these topological considerations in order to throw light on the question of the relative magnitude of calculated "ring-current" intensities in large, polycyclic molecules. This process will invoke the mathematical techniques of Graph Theory, the basic ideas of which are briefly introduced in the present chapter; they will then be applied, in Chapter VI, to emphasise which aspects of "ring-current" calculations are topological in nature, and which are not; finally, in Chapter VII, topological (though not, specifically, graph-theoretical) ideas will be used to rationalise the relative magnitudes of "ring-current" intensities calculated, on the basis of the London-McWeeny method, in an arbitrary, conjugated hydrocarbon. We first consider some graph-theoretical definitions.

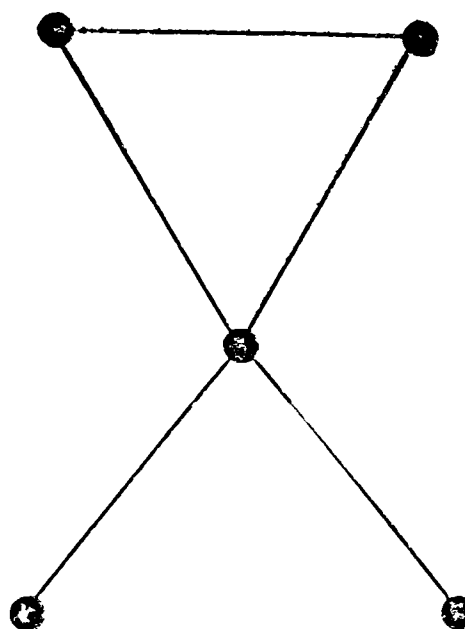
5.2 Elements of Graph Theory: Definitions and Terminology

The terminology of graph theory is, unfortunately, very non-uniform, varying considerably, as it does, from one author to another. In this section we give, without excessive rigour or formality, a consistent

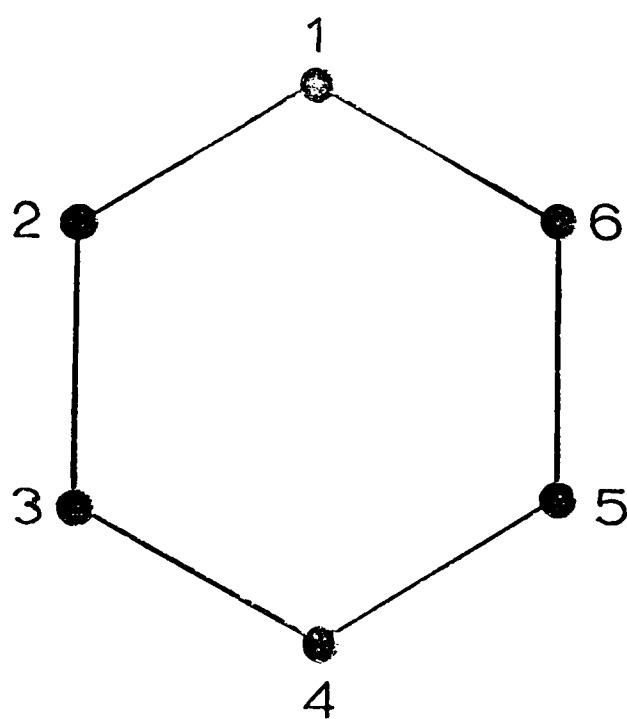
FIGURE 5.1



(a)



(b)



(c)

Various Graphs Illustrating the Definitions Given in §§5.2 (ii)
and 5.2 (iii)

nomenclature which will be used in the subsequent discussion in this Thesis.*

(i) Graph, Vertex, Edge, Degree

For our purposes, a graph G may be defined as a pair $(V(G), E(G))$, where $V(G)$ is a non-empty set of elements called vertices, and $E(G)$ is a finite set of unordered pairs of distinct elements of $V(G)$, called edges. Diagrammatically (and more heuristically) a graph may be represented by a set of labelled points (the vertices), which are either 'joined' or 'not joined' by lines (the edges) — where vertex i of G is said to be 'joined' to vertex j of G if the element $\{i, j\}$ is contained in $E(G)$. As an example of the above definition, the diagrams shown in Figure 5.1 are graphs as defined. Note that here, as in all the graphs with which we shall be concerned, there is never more than one edge joining a given pair of vertices, and each vertex is joined to at least one other (the actual number, $\rho(i)$, of edges incident upon any vertex i is called the degree of this vertex). It is immediately evident that a conjugated system (benzene, for example, Figure 5.1c) may be represented as a simple graph, in which the carbon atoms correspond to vertices (the hydrogen atoms are neglected) and the carbon-carbon sigma-bonds correspond to edges. (In the succeeding discussion, the terms 'atoms' and 'vertices' will frequently be used indiscriminately and inter-changeably, as will the terms 'bonds' and 'edges').

(ii) Vertex Adjacency-Matrix, Characteristic Polynomial, Characteristic Equation, Eigenvalues, Eigenvectors and Spectrum of a Graph

Once the vertices of a graph G (comprising N vertices) have been (arbitrarily) labelled as described above, the corresponding vertex

* Standard texts on graph theory are the books by Harary,³⁰⁵ Berge³⁰⁶, and Wilson³⁰⁷, while a very rigorous and consistent set of definitions and terminology has recently been given by Rigby³⁰⁸.

adjacency-matrix of G is defined to be the real, symmetric $N \times N$ - matrix $A(G) (= [a_{ij}])$ in which $a_{ij}=1$ if vertices i and j are joined and $a_{ij}=0$ if the same vertices are not joined; the diagonal elements are also zero. The adjacency matrix of the graph in Figure 5.1a, for example, is

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 1 \\ 0 & 1 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix}$$

The characteristic polynomial, $P(G;\lambda)$, of a graph G is the characteristic polynomial of an ^{*} adjacency matrix of G . As with any square matrix, this is obtained by subtracting from $A(G)$ the unit matrix, of the appropriate dimension (N), multiplied by the scalar ^{**} λ , and then evaluating the

* Note that deliberate reference has been made here to 'an adjacency matrix of G ' rather than to 'the adjacency matrix of G ', for each distinct labelling of the vertices of G gives rise to a superficially different (though isomorphically equivalent) adjacency-matrix. It can be shown, however (e.g. refs. 305-307), that the characteristic polynomial of G (and hence the characteristic equation and the eigenvalues of G) rest unchanged under such relabellings; these quantities are therefore said to be graph invariants, and therein lies their importance in Graph Theory.

** i.e. by subtracting what Sir Arthur Cayley, in his original (1858) Memoir on the Theory of Matrices³⁰⁹, more succinctly called "the single quantity λ considered as involving the matrix unity" — a convenient terminology which seems to have fallen into disuse.

determinant of the resulting matrix - i.e.

$$\begin{aligned} P(G; \lambda) &= |\mathbb{A}(G) - \lambda \mathbb{I}_{N \times N}| \\ &= (-1)^N \lambda^N + a_1 \lambda^{N-1} + a_2 \lambda^{N-2} + \dots + a_N \end{aligned} \quad (5.1)$$

The degree of this polynomial is therefore obviously numerically equal to the number of vertices in the graph; setting $P(G; \lambda) = 0$ yields the characteristic equation of G . The roots, $\{\lambda_i\}_{i=1,2,\dots,N}$, of this equation are then the N (not-necessarily-distinct) eigenvalues of G . The corresponding eigenvectors, $\{\tilde{v}_i\}_{i=1,2,\dots,N}$, of $\mathbb{A}(G)$ are the N eigenvectors of G — i.e., they are the vectors $\tilde{v}_i$ with the property

$$\mathbb{A}(G) \tilde{v}_i = \lambda_i \tilde{v}_i \quad (5.2),$$

where λ_i is one of the eigenvalues of G . The family of N eigenvalues of $\mathbb{A}(G)$, $\{\lambda_i\}_{i=1,2,\dots,N}$, is called the spectrum of G .

Note that because $\mathbb{A}(G)$ is always a real-symmetric matrix all eigenvalues of G are real, and eigenvectors of G belonging to distinct eigenvalues are automatically mutually orthogonal.

(iii) Path, Path-Length, Circuit, Connectedness and Components

A path within a graph G with vertex set $\{V_1, V_2, \dots, V_N\}$, is a finite, non-empty sequence of distinct vertices of the form $\{V_1 \rightarrow V_2\}, \{V_2 \rightarrow V_3\}, \dots, \{V_{p-1} \rightarrow V_p\}$ in which two consecutive edges are adjacent (i.e., have a vertex in common). This can also be represented $V_1 \rightarrow V_2 \rightarrow \dots \rightarrow V_{p-1} \rightarrow V_p$. (The length of a path is the number of edges it comprises). If, however, $V_1 = V_p$, the edge sequence in question is called a circuit. For example, in Figure 5.1a, $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$ is a path, and $2 \rightarrow 3 \rightarrow 4 \rightarrow 2$ is a circuit. In the

graph shown in Figure 5.1c, $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 6$ is a path, but $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 6 \rightarrow 1$ is a circuit.

A graph in which any two vertices are joined by a path is a connected graph. The graphs in Figure 5.1 are connected graphs — as, in fact, will be all graphs which represent single molecules. A graph which is not connected consists of two or more components, each of which is a connected graph.

(iv) Hamiltonian Graphs

If, in a graph G , there exists a circuit which passes once, and once only, through each vertex of G — such a circuit being called a Hamiltonian circuit, or, sometimes, a spanning cycle — then G is said to be a Hamiltonian graph; otherwise, G is non-Hamiltonian. If G contains a path which passes through each one of its vertices — that is to say, if G contains a spanning path — then G is path-Hamiltonian. Such a spanning path will also often be referred to subsequently as a Hamiltonian path. Of the graphs depicted in Figure 5.1, that in Figure 5.1a is path-Hamiltonian (though not Hamiltonian) — it is path-Hamiltonian between vertices 1 and 4 (i.e., it is '(1,4)-path-Hamiltonian') along $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$; that in Figure 5.1c is Hamiltonian (a Hamiltonian circuit being $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 6 \rightarrow 1$); that in Figure 5.1b is neither Hamiltonian nor path-Hamiltonian. (The graph in Figure 5.1b may therefore be more concisely described as being non-path-Hamiltonian for, evidently, a Hamiltonian graph must also be path-Hamiltonian.)

(v) Trees, Spanning Trees, Circuit Rank, and

Fundamental System of Circuits

A connected graph which contains no circuits is called a tree. If, in a graph which contains circuits, one edge is successively removed from

each circuit until there are no circuits left, the graph remaining is a tree (since a connected graph is a tree if and only if it contains no circuits) and, furthermore, it connects all the vertices of G ; it is thus called a spanning tree of G . The number of edges removed during this process (*i.e.* the number of 'independent' circuits in the graph — analogous to the number of 'rings' in a polycyclic molecule) is called the circuit rank of G . The fundamental system of circuits of a spanning tree is obtained by taking a spanning tree T , of G , and adding, separately, one-by-one, the edges of G not contained in T . Each such addition produces a unique circuit (see ref. 307, p.47) and the set of all such circuits formed in this way is called the fundamental system of circuits of T ; the number of distinct circuits in such a system is, of course, again equal to the circuit rank of G . Examples illustrating these ideas will arise later in the discussion of §6.3.

5.3 Equivalence of the Adjacency Matrix and the Hückel Hamiltonian-Matrix

(i) Hydrocarbons Treated via the Simplest HMO-Approach

In this section it will be shown, somewhat informally and intuitively by means of a specific example, that the Hückel Hamiltonian-matrix for a conjugated hydrocarbon-system is isomorphic with a vertex adjacency-matrix of the graph which represents the carbon-carbon sigma-bond connectivity of the species in question. The discussion given here is based closely on §2.7 and Appendix A* of the author's recent book with Coulson and O'Leary³¹⁰; the reader requiring more-rigorous and formal justification of the isomorphism under consideration is referred to refs. 311-313.

* N.B. These particular parts of the above book were written solely by the present author.

The example we consider is butadiene, the sigma-bond connectivity of which may conveniently be depicted schematically as in Figure 5.2; this figure shows the reduction of both cis- and trans-butadiene to their equivalent

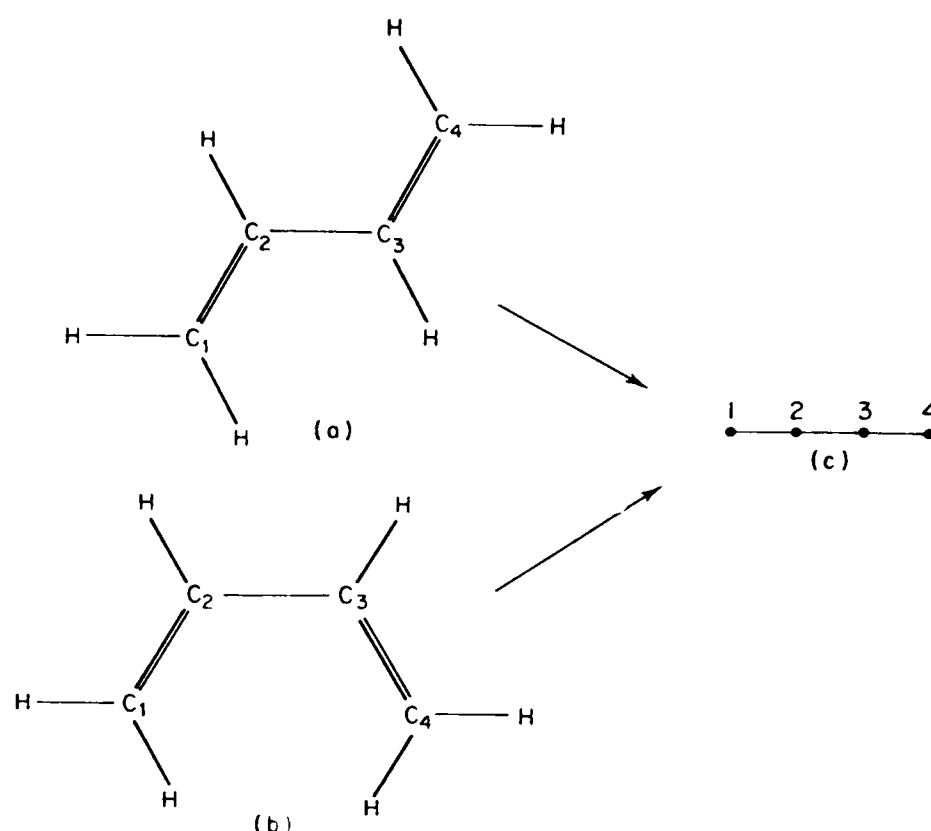


FIGURE 5.2

graph which thus illustrates the carbon-carbon sigma-bond connectivity of both forms of butadiene. This emphasises what has long been intuitively evident to anyone who has ever carried out an HMO-calculation, namely that Hückel theory is concerned only with the sigma-bond connectivity of a conjugated system and not with molecular geometry. The Hückel Hamiltonian-matrix (in the usual α, β -notation) for butadiene, with the vertex labelling adopted in Figure 5.2, is³¹⁰ :

$$H(\text{butadiene}) = \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \quad (5.3)$$

In the zero-overlap case, the secular determinant is $|\mathbf{H} - \epsilon \mathbf{I}|_{4 \times 4}$ (butadiene) and so the secular equations lead to:

$$\begin{vmatrix} \alpha - \epsilon & \beta & 0 & 0 \\ \beta & \alpha - \epsilon & \beta & 0 \\ 0 & \beta & \alpha - \epsilon & \beta \\ 0 & 0 & \beta & \alpha - \epsilon \end{vmatrix} = 0 \quad (5.4)$$

At this point it is conventional to divide each element of the determinant by β (since we are dealing with a zero determinant, this is perfectly permissible) to obtain

$$\begin{vmatrix} \frac{\alpha - \epsilon}{\beta} & 1 & 0 & 0 \\ 1 & \frac{\alpha - \epsilon}{\beta} & 1 & 0 \\ 0 & 1 & \frac{\alpha - \epsilon}{\beta} & 1 \\ 0 & 0 & 1 & \frac{\alpha - \epsilon}{\beta} \end{vmatrix} = 0 \quad (5.5)$$

and to measure energy with reference to α (i.e. to take the Coulomb integral, α , as the energy zero) and in units of β (i.e. to set

$$x = \frac{\epsilon - \alpha}{\beta} \quad (5.6)$$

The secular determinant for butadiene then becomes

$$\begin{vmatrix} -x & 1 & 0 & 0 \\ 1 & -x & 1 & 0 \\ 0 & 1 & -x & 1 \\ 0 & 0 & 1 & -x \end{vmatrix} = 0 \quad (5.7)$$

If we now consider the vertex adjacency-matrix (as defined in §5.2(ii)) of the molecular graph of butadiene shown in Figure 5.2(c), as labelled in that figure, this matrix is found to be

$$\mathbb{A}_{\text{(butadiene)}} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad (5.8)$$

The eigenvalues of $\mathbb{A}(G)$ are, by definition (§5.2(ii)), the roots of

$$\left| \mathbb{A}(G) - \lambda \mathbb{I}_{N \times N} \right| = 0 \quad (5.9)$$

in which $\mathbb{I}_{N \times N}$ is the unit matrix of dimension N . In the case of the butadiene example, on substitution of $\mathbb{A}_{\text{(butadiene)}}$ (equation (5.8)) for $\mathbb{A}(G)$ in (5.9), this latter equation becomes:

$$\begin{vmatrix} -\lambda & 1 & 0 & 0 \\ 1 & -\lambda & 1 & 0 \\ 0 & 1 & -\lambda & 1 \\ 0 & 0 & 1 & -\lambda \end{vmatrix} = 0 \quad (5.10)$$

Comparison of equations (5.7) and (5.10) shows that when energies are expressed relative to α , and in units of β , the Hückel Hamiltonian-matrix

for a given conjugated-hydrocarbon is isomorphic with (and, in the zero-overlap approximation, identical to) the vertex adjacency-matrix of the correspondingly labelled graph. This correspondingly labelled graph represents the sigma-bond connectivity of the atoms comprising the conjugated system in question. Since, when energies are expressed relative to α , and in units of β (i.e. when α is set at 0, and β is set at 1),

$\mathbb{A}(G) = \mathbb{H}(\text{molecule})$, in the zero-overlap case (cf. equations (5.3) and (5.8)), we have that $\{\lambda_I\}_{I=1,2,\dots,N}$, the eigenvalues of $\mathbb{A}(G)$ (the roots of (5.9)) are identical to $\{x_I\}_{I=1,2,\dots,N}$, the roots of the appropriate Hückel secular-determinant. In addition, the MO-energies, $\{\epsilon_I\}_{I=1,2,\dots,N}$, are simply and directly related to the $\{x_I\}$, via the (constant and empirical) parameters α and β , as in equation (5.6)

Finally, since $\mathbb{H}(\text{molecule})$ and $\mathbb{A}(G)$ commute (i.e.

$$\mathbb{H}\mathbb{A} - \mathbb{A}\mathbb{H} = \mathbb{O} \quad (5.11)$$

they also have the same eigenvectors; but the eigenvector of $\mathbb{H}(\text{molecule})$, $\{c_{Ir}\}_{r=1,2,\dots,n}$, corresponding to the eigenvalue x_I , is the set of LCAO-combinatorial-coefficients associated with the I^{th} MO, and hence these also are a function only of $\mathbb{A}(G)$, and thus only of the carbon-atom connectivity of the molecule in question.

These observations all emphasise that in the simple HMO-approach for hydrocarbons,

- 1) the MO energy-levels and,
- 2) the LCAO-combinatorial coefficients

are determined solely and entirely (to within the parameters α and β) by the carbon-atom connectivity — this is often (but somewhat unfortunately) called the 'topology' — of the conjugated system under investigation.

(ii) Heteroconjugated Systems

These analogies may be extended to heteroconjugated systems if the definition of the adjacency matrix given in §5.2(ii) is generalised sufficiently in order to describe the vertex-connectivities of graphs which are more appropriate for representing conjugated systems containing hetero-atoms. These are the so-called weighted graphs^{314-318, 308} in which, to each edge, joining vertices i and j , is assigned an edge weighting, $k_{ij} = k_{ji}$, and to each vertex, r , is assigned a vertex weighting,^{*} h_r . The r^{th} -element along the diagonal of the adjacency matrix which represents this edge- and vertex-weighted graph is thus h_r instead of zero (which is what it was in the vertex adjacency-matrix of the correspondingly labelled unweighted graph — see §5.2(ii)); the off-diagonal elements a_{ij} — which, in the adjacency matrix of the corresponding unweighted graph, were all either 1 or 0 according as to whether there was, or was not (respectively), an edge joining the vertices i and j — are now k_{ij} . (Two vertices unconnected by any edge could thus in general still be regarded as being joined — but by an edge of zero weighting.)

Now, in the simple HMO-scheme, if the r^{th} carbon-atom in a conjugated hydrocarbon is replaced by a hetero-atom, the (r,r) -element of the Hückel Hamiltonian-matrix changes from α to α_r , where³¹⁹

$$\alpha_r = \alpha + h_r \beta. \quad (5.12)$$

* On another convention, instead of a vertex weighting's being assigned as described above, a loop (r,r) is drawn on the r^{th} vertex, which is then (also) given an edge weighting, k_{rr} . These distinctions, and the pros and cons of each scheme, are outside the scope of the present discussion, but, in another context, they have been the concern of the present author, and the interested reader is referred to refs. 314-318, and 308.

h_r therefore reflects the difference, in units of β , between the Coulomb integral of a carbon atom in benzene and that (α_r) thought, by some criteria, to be appropriate, in Hückel theory, for the type of hetero-atom that is in position r . Clearly, from equation (5.6), when energies are measured relative to α , and in units of β , α_r becomes numerically equal to h_r and hence, under these conditions, the (r,r) -element of the Hückel Hamiltonian-matrix of the conjugated system under study will be h_r — exactly the same as the corresponding diagonal-element of the adjacency matrix of the similarly labelled weighted-graph which represents the conjugated molecule in question. Likewise, the resonance integral between two different types of atoms, i and j , is³¹⁹

$$\beta_{ij} = k_{ij}\beta \quad (5.13)$$

where k_{ij} is some semi-quantitative (and partially subjective) measure of the electron-attracting propensity of the i - j bond³¹⁰; and when β is set equal to unity (i.e. β is taken to be the unit of energy), β_{ij} (the (i,j) -entry in the Hückel Hamiltonian-matrix for the heteroconjugated system under discussion) will be numerically equal to k_{ij} (the weighting of the edge joining vertices i and j in the correspondingly labelled edge- and vertex-weighted graph).

Hence, by admitting these arbitrarily edge- and vertex-weighted graphs, an isomorphism may always be established between the adjacency matrices of appropriate graphs of this class and the Hückel Hamiltonian-matrices of heteroconjugated molecules having any number of different Coulomb- and resonance integrals.

5.4 Sub-Graph Techniques for Evaluating the Characteristic Polynomial of a Graph

In this Thesis, whenever the eigenvalues of a molecular graph are required, they will be obtained numerically by the standard, Jacobean, computer matrix-diagonalisation method. For completeness, however, we make brief reference here to the several sub-graph techniques³²⁰⁻³²⁶ for evaluating the characteristic polynomial of a graph, extensions of which to edge- and vertex-weighted graphs have recently been the subject of intense study³¹⁴⁻³¹⁸ — not least by the present author.^{314-316,318.}

The coefficients, a_i , of the characteristic polynomial, $P(G;\lambda)$, of a simple graph without weighted edges or vertices are usually evaluated by use of a formula due to Sachs³²⁴; all the other available methods³²⁰⁻³²⁵ may be shown³²⁷ to be equivalent to, or at least related to, Sachs' formula.

In the Sachs method a_i is evaluated by picking out all sub-graphs^{*} of the original graph on i vertices, the components of which may only be either (or both) of the following

(a) Two vertices joined by a single edge $(\bullet \text{---} \bullet)$

(b) Closed cycles of vertices $(\bullet \text{---} \bullet \text{---} \bullet \text{---} \bullet \text{---} \bullet)$

Such sub-graphs are often referred to as Sachs graphs³²⁸ or, more appropriately, mutation graphs^{329,308,318}. (Note also that the empty graph counts as a mutation graph for this purpose)

* A graph $(V(G^{\text{sub}}), E(G^{\text{sub}}))$ is a subgraph of $(V(G), E(G))$ if, and only if, $V(G^{\text{sub}}) \subset V(G)$ and $E(G^{\text{sub}}) \subset E(G)$.

The Sachs theorem³²⁴ then asserts that

$$a_{N-i} = \sum_{s \in S_i} (-1)^{c(s)} 2^{r(s)} \quad (5.14)$$

where $c(s)$ is the number of components in the particular Sachs graph s , on i vertices, currently under consideration, and $r(s)$ is the number of rings in that subgraph; the summation is over all such Sachs graphs on i vertices. In addition $a_0 = 1$, by definition.

The method is illustrated³³⁰ by setting up the characteristic polynomial of the molecular graph of methylene cyclopropane (Figure 5.3). Hence

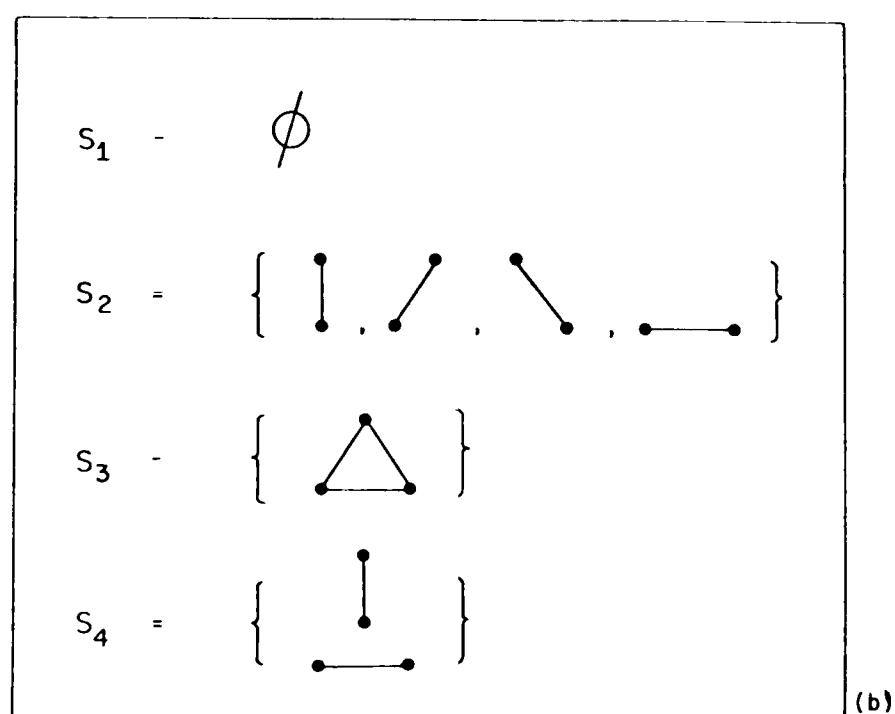
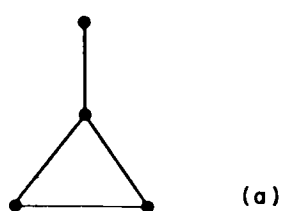


FIGURE 5.3

$$a_0 = 1$$

$$a_1 = 0$$

$$a_2 = (-1)^1 2^0 + (-1)^1 2^0 + (-1)^1 2^0 + (-1)^1 2^0 = -4$$

$$a_3 = (-1)^1 2^1 = -2$$

$$a_4 = (-1)^2 2^0 = 1$$

(5.15)

and the characteristic polynomial of this graph is thus

$$P(G;\lambda) = \lambda^4 - 4\lambda^2 - 2\lambda + 1 \quad (5.16)$$

By extending the concept of what constitutes a mutation graph, other workers³¹⁴⁻³¹⁸ (including the present author^{314-316,318}) have generalised Sachs' formula to enable the characteristic polynomial of an arbitrarily edge- and vertex-weighted graph to be obtained by inspection of appropriate sub-graphs contained within it.

$P(G;\lambda)$ not only implicitly contains information about the eigenvalue spectrum of G , but it also gives insight into the nature of the graph spectrum—for example, the famous Coulson-Rushbrooke theorem¹⁰, and extensions^{316,331} to it, may be deduced in this way^{312,313,316,328,330,331}. It should be pointed out, however, that, despite its name, the so-called characteristic polynomial of a graph does not characterise it up to isomorphism³³²⁻³³⁵; this 'isospectral problem' has been the subject of some recent work by the present author³³⁵, but it is not further discussed here as it does not appear to have significant application in the context of "ring-current" theories.

Now that the relevant graph-theoretical terminology has been established, we are in a position to consider specifically, in Chapter VI, the graph-theoretical aspects of "ring-current" calculations on conjugated systems.

CHAPTER VI

SOME GRAPH-THEORETICAL ASPECTS OF SIMPLE "RING-CURRENT" CALCULATIONS ON CONJUGATED SYSTEMS

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CHAPTER VI

SOME GRAPH-THEORETICAL ASPECTS OF SIMPLE "RING-CURRENT"
CALCULATIONS ON CONJUGATED SYSTEMS*6.1 Summary and Scope of the Chapter

In this chapter, we shall examine the simple London-Pople-McWeeny theory of π -electron "ring-currents", with particular reference to the topological or graph-theoretical aspects of it. As was discussed in the previous chapter, there is a close correspondence between the adjacency matrix of the graph representing the sigma-bond skeleton of the carbon atoms comprising a given conjugated-system, and the secular equations which arise in the theory (a relationship now known — see §5.3 — to be common to all formalisms based on Hückel 'topological' molecular-orbitals), but in addition we shall emphasise here that several other graph-theoretical ideas — notably those concerning circuits and spanning trees — specifically underlie the "ring-current" concept. In this connection, the question of whether or not any given molecular-graph is path-Hamiltonian is of prime importance, and it will be pointed out that the unitary transformation originally proposed by McWeeny¹³² applies to path-Hamiltonian molecular-graphs, whereas one recently devised by Gayoso and Boucekkine^{165a} can be applied to any simple, connected graph — as also can the explicit "ring-current" formula (equation (3.33)) presented in §3.6. These ideas will be illustrated by some simple numerical-calculations, and an example will be

* The material presented in this chapter has now been published.

The full reference is:

R.B. MALLION, "Some Graph-Theoretical Aspects of "Ring-Current" Calculations on Conjugated Systems", Proceedings of the Royal Society (London), 1975,

Vol. A341 (Mathematics and Physical Sciences), pp. 429-449.

given of a conjugated system (decacyclene) whose molecular graph is apparently non path-Hamiltonian. We shall conclude by emphasising that although much graph theory is inherent in the "ring-current" concept, the "ring-current" index itself is not a completely topological quantity — even when a purely topological wave-function (such as the simple Hückel one) has been used to calculate it.

6.2 Introduction

We saw in the last chapter how the very simplest molecular-orbital calculations which have long been performed on planar, conjugated hydrocarbons are purely topological and graph-theoretical in nature. Such graph-theoretical ideas have even been used in the wider context of three-dimensional systems³³⁶. In particular, however, as was emphasised in Chapter V, when the Hückel MO-method is applied in its most elementary form to planar hydrocarbons, the secular equations, energy levels and coefficients which arise all have exact counterparts in pure graph theory; these are, respectively, the characteristic equation, eigenvalues and eigenvectors of the adjacency matrix of the graph representing the sigma-bond skeleton of the atoms comprising a given conjugated-system. (See §5.2 for definitions of these quantities.) Many of the numbers which emerge from simple HMO-calculations are, therefore, solely dependent on molecular topology, and such elegant MO-theorems as, for example, the 'pairing theorem' of Coulson and Rushbrooke¹⁰ are, in essence, purely graph theoretical.

The present chapter is intended to emphasise specifically the graph-theoretical implications peculiar to those calculations in which such a rudimentary, purely topological, MO-theory is applied to determine the magnetic properties of planar, conjugated systems which contain cycles of atoms. These are the systems, the subject of the present Thesis, which are often spoken of as being capable of supporting " π -electron ring-currents"

when a non-zero component of an external magnetic-field is extant, perpendicular to the plane in which the cycles of atoms are situated. It is, perhaps, not surprising that the theory of circuits and spanning trees plays an important (though often implicit) rôle in such calculations, and we shall see that the question of whether a Hamiltonian path, or only a branched spanning-tree, can be devised within the graph representing any particular conjugated-molecule, is also of relevance.

6.3 Graph-Theoretical Aspects of "Ring-Current" Theory

(i) Perturbation of the Secular Determinant by an Applied Magnetic-Field

We recall from §1.4(i)(i) that the effect of a uniform, external magnetic-field, with a component perpendicular to the plane of the molecule, is to perturb the original 'field-free' Hückel secular-determinant by modifying all the off-diagonal matrix-elements, h_{ij} , in the original AO-basis, by a complex factor

$$\omega_{ij} = \exp(i\theta_{ij}), \text{ where}$$

$$\theta_{ij} = 2\pi \left[\frac{e}{h} \right] S_{ij} B_0 \quad (6.1)$$

in which the symbols have the same meaning as they had in §1.4(i). Clearly,

$$|\omega_{ij}| = 1 \text{ and, since } S_{ij} \text{ is a signed area, } S_{ji} = -S_{ij} \text{ and therefore}^\dagger$$

$$\omega_{ji} = \omega_{ij}^*.$$

[†] When "ring-current" chemical-shifts are to be calculated, the definition of θ_{ij} given in equation (6.1) is often modified by the addition of a term involving the magnetic moment of an infinitesimal 'test'-dipole, as in equation (1.84). This procedure was discussed in Chapter III. The main point to note here is that this additional dipole-term in θ_{ij} is also multiplied by the $S_{ij}(= -S_{ji})$ factors, and hence, even with this modified definition of θ_{ij} , it is still true that $\omega_{ji} = \omega_{ij}^*$; all the analysis outlined in the text therefore still applies, even when this 'test-dipole' term is included in the definition of θ_{ij} .

(ii) McWeeny's Unitary-Transformation for Path-HamiltonianGraphs Containing Circuits

Using this formulation, London³, Pople¹³¹ and McWeeny¹³² have shown that for the perturbation just described to have a non-zero effect, the conjugated system must comprise what are often loosely described as "closed circuits" of atoms — i.e., in our present terminology, the graph representing its sigma-bond topology (which will subsequently be called its 'molecular graph') must have circuit rank ≥ 1 . We here consider McWeeny's demonstration, for it is the one which illustrates most clearly the graph-theoretical ideas underlying the "ring-current" concept.

In the course of his proof, McWeeny¹³² performed an elegant unitary-transformation on the basis orbitals, making, for simplicity, what amounted to an assumption that the conjugated system in question has a molecular graph which is path-Hamiltonian; for, if this is so, it is then possible to number the atoms (vertices) "along any chain which is continuous and open" as McWeeny prescribed, (the "actual molecule" then being "completed by . . . further links, one in each ring").¹³²

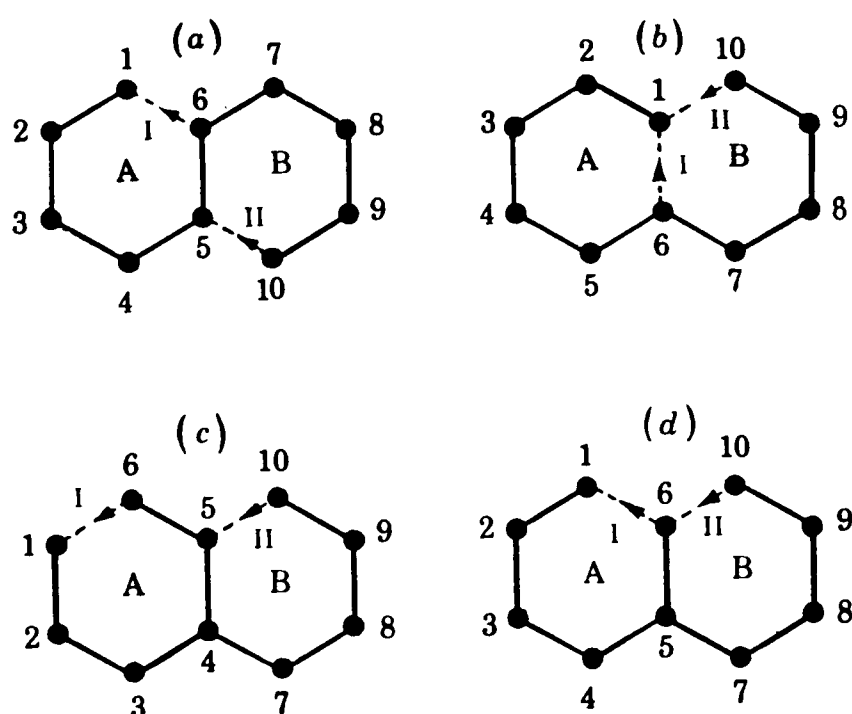


FIGURE 6.1

The Hamiltonian paths used by McWeeny for his calculation on the naphthalene molecule are shown in Figures 6.1a and 6.1b. It should be noted first of all that the molecular graph for naphthalene is a Hamiltonian graph of circuit rank 2. The semi-Hamiltonian chains shown in Figures 6.1a and 6.1b are, furthermore, spanning trees of the naphthalene molecular graph; each spanning tree will have associated with it the unique fundamental system of circuits (two in this case), the appropriate edges ('bonds') requiring to be added being 6-1 and 10-5 for the tree in Figure 6.1a, and 6-1 and 10-1 for that in Figure 6.1b.

Then, considering such a semi-Hamiltonian chain with the atoms numbered sequentially and letting $\bar{h}$ be the matrix of the perturbed Hamiltonian (in the usual quantum-mechanical usage of this word) in the original AO-basis, McWeeny effected the unitary transformation

$$\bar{h} = U^\dagger h U \tag{6.2}$$

in which U is a diagonal matrix

$$U = \text{diag} (\omega_{11}^*, \omega_{11}^* \omega_{12}^*, \omega_{11}^* \omega_{12}^* \omega_{23}^*, \omega_{11}^* \omega_{12}^* \omega_{23}^* \omega_{34}^* \dots) \tag{6.3}$$

with general element

$$U_{ii} = \omega_{11}^* \omega_{12}^* \omega_{23}^* \dots \omega_{i-1,i}^* \tag{6.4}$$

When this transformation has been applied, all the near-diagonal ω_{ij} -elements are transformed to unity (i.e. revert to the 'field-free' form), but ω_{61} , for example, in the matrix representing chain (a) in Figure 6.1, is replaced by

$$\bar{\omega}_{61} \equiv U_{66}^{\dagger} \omega_{61} U_{11} = \omega_{12} \omega_{23} \omega_{34} \omega_{45} \omega_{56} \omega_{61} \quad (6.5)$$

and $\omega_{10,5}$ is transformed to a product of similar terms taken around the second ring

$$\bar{\omega}_{10,5} \equiv U_{10,10}^{\dagger} \omega_{10,5} U_{55} = \omega_{56} \omega_{67} \omega_{78} \omega_{89} \omega_{9,10} \omega_{10,5} \quad (6.6)$$

When transformation (6.2), with U defined in (6.3), is applied to the tree of Figure 6.1b, ω_{61} again goes to $\bar{\omega}_{61}$ given by equation (6.5), but $\omega_{10,1}$ is now $\bar{\omega}_{10,1}$, where

$$\begin{aligned} \bar{\omega}_{10,1} &\equiv U_{10,10}^{\dagger} \omega_{10,1} U_{11} \\ &= \omega_{12} \omega_{23} \omega_{34} \omega_{45} \omega_{56} \omega_{67} \omega_{78} \omega_{89} \omega_{9,10} \omega_{10,1} \end{aligned} \quad (6.7)$$

i.e. a product of terms taken around that circuit of the molecular graph which insertion of the edge 10-1 (only), in the spanning tree 6.1b, completes (in this case, it is a 'two-ring' circuit).

In this way, McWeeny's transformation showed that all the perturbation resulting from the presence of the external magnetic-field can be thought of as being concentrated in only one bond (edge) of each ring (fundamental circuit) of a (poly) cyclic molecule (molecular graph of circuit rank ≥ 1) and that, in the absence of these 'closed cycles' of atoms (i.e. if the molecular graph has circuit-rank zero), the field has no effect — thus confirming the earlier results of London¹ and Pople¹³².

(iii) Gayoso and Boucekkine's Unitary-Transformation for
Non-Path-Hamiltonian Graphs Containing Circuits

Although, as is evident from the above discussion, McWeeny's unitary-transformation applies only to path-Hamiltonian molecular-graphs, we shall show that the result of the transformation still holds, even when it is based on a spanning tree containing no Hamiltonian paths. Two such spanning trees for the naphthalene molecular-graph are shown in Figures 6.1c and 6.1d. To deal with this type of situation — and, in particular (although they did not actually express it in this way) for systems whose molecular graphs themselves are actually non path-Hamiltonian, and whose vertices (atoms) cannot, therefore, form a spanning path — Gayoso and Boucekkine^{165a} proposed a further unitary-transformation which generalises the one devised by McWeeny. In this approach, any arbitrary spanning-tree is selected (in general one through which no Hamiltonian path can be drawn — e.g. Figures 6.1c and 6.1d) and the vertices (atoms) are numbered, starting from an arbitrary vertex which is labelled 1, the others being labelled a,b,c,...f...i,j,k,...x,y,... in any order whatever. Then, the matrix used to carry out transformation (6.2) is again diagonal, but its i^{th} element now has the form

$$U_{ii} = \omega_{1l}^* \omega_{lf}^* \omega_{fk}^* \cdot \cdot \cdot \omega_{xi}^* \quad (6.8)$$

where (lf) (fk) ... (xi) is a sequence of edges representing the shortest path between the vertex labelled 1, and that labelled i. Now, when the unitary transformation (6.2) has been applied to the original matrix of the perturbed Hamiltonian, the only non-zero ω_{ij} -terms which are not transformed identically to unity are again the ones corresponding to those edges of the complete molecular-graph (joining pairs of vertices i and j) which must be

added to the particular spanning-tree on which the transformation is being based, in order to re-form its fundamental system of circuits — that is to say, the ω_{ij} 's for what McWeeny called the "circuit-completing bonds".

As an illustration of this more-general transformation, we shall apply it to the branched spanning-tree shown in Figure 6.1c. ω_{61} again becomes $\bar{\omega}_{61}$ as in the previous example (equation (6.5)); for the element corresponding to the other 'circuit-completing' edge, (10,5), we consider:

$$\bar{\omega}_{10,5} \equiv U_{10,10}^{\dagger} \omega_{10,5} U_{55} \quad (6.9)$$

Now, the shortest path from vertex 1 to vertex 5 is clearly just $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5$. Therefore:

$$U_{55} = \omega_{11}^* \omega_{12}^* \omega_{23}^* \omega_{34}^* \omega_{45}^* \quad (6.10)$$

whilst the shortest path (in the spanning tree of Figure 6.1c) between vertices 1 and 10 is evidently $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 7 \rightarrow 8 \rightarrow 9 \rightarrow 10$. Thus,

$$U_{10,10}^{\dagger} \equiv \omega_{11} \omega_{12} \omega_{23} \omega_{34} \omega_{47} \omega_{78} \omega_{89} \omega_{9,10} \quad (6.11)$$

Therefore, from (6.9) - (6.11),

$$\begin{aligned} \bar{\omega}_{10,5} &= (\omega_{11} \omega_{12} \omega_{23} \omega_{34} \omega_{47} \omega_{78} \omega_{89} \omega_{9,10}) \omega_{10,5} \\ &\quad (\omega_{11}^* \omega_{12}^* \omega_{23}^* \omega_{34}^* \omega_{45}^*) \end{aligned} \quad (6.12)$$

which, since $\omega_{ij} \omega_{ij}^* = 1$, gives

$$\begin{aligned}
 \bar{\omega}_{10,5} &= \omega_{45}^* \omega_{47} \omega_{78} \omega_{89} \omega_{9,10} \omega_{10,5} \\
 &= \omega_{54} \omega_{47} \omega_{78} \omega_{89} \omega_{9,10} \omega_{10,5}
 \end{aligned}
 \tag{6.13}$$

Again, therefore, the original $\omega_{10,5}$ is, after the unitary transformation, replaced by a product of ordered ω_{ij} -terms taken around the circuit which edge (10,5) completes, in the particular spanning-tree (that in Figure 6.1c) selected as a basis for the transformation; once more, however, the ω_{ij} 's where (i,j) is an edge of the spanning tree, are transformed to unity.

$$\begin{aligned}
 \bar{\omega}_{34} &\equiv U_{33}^\dagger \omega_{34} U_{44} \\
 &= (\omega_{11} \omega_{12} \omega_{23}) \omega_{34} (\omega_{11}^* \omega_{12}^* \omega_{23}^* \omega_{34}^*) \quad . \\
 &= 1
 \end{aligned}
 \tag{6.14}$$

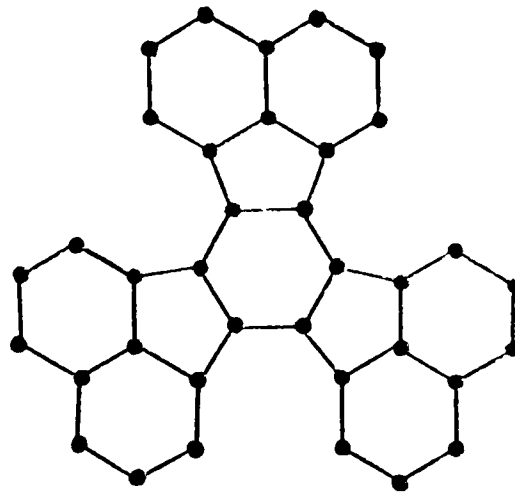
(iv) Path-Hamiltonian and Non-Path-Hamiltonian Molecular-Graphs

The question of whether a given calculation is to be based on a branched or non-branched spanning-tree is something of an academic one in the case of a conjugated system like naphthalene whose molecular graph is Hamiltonian (and, therefore, path-Hamiltonian — the strongest requirement which the McWeeny transformation demands); since a path-Hamiltonian spanning-tree can always be devised within such a graph, no practical advantage is to be gained by considering the matter further. The Gayoso-Boucekkine transformation comes into its own, however, when consideration is given to a calculation of the magnetic properties of those conjugated systems whose molecular graphs are non path-Hamiltonian.

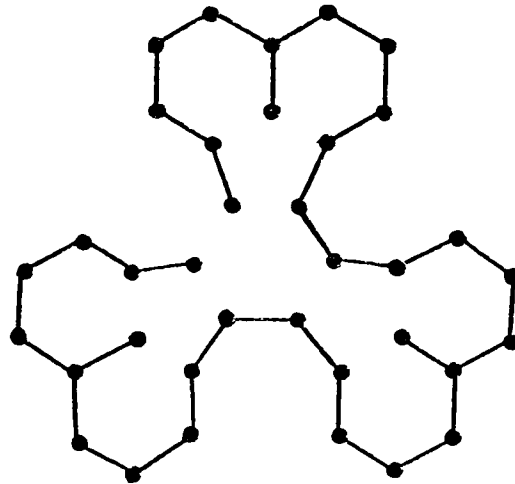
In making such an apparently innocent statement we are, however, immediately in difficulties; for, surprising as it may seem, initially, the question of prescribing a set of necessary and sufficient conditions for a

FIGURE 6.2

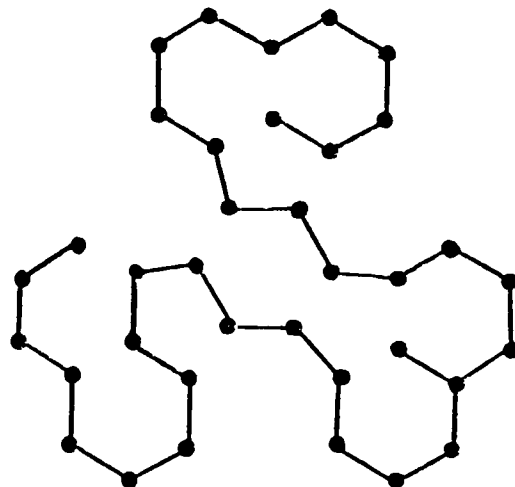
a)



b)



c)



The Decacyclene Molecular-Graph, and Two of its
Spanning Trees

graph to be Hamiltonian (or just path-Hamiltonian) is one of the major unsolved-problems of Graph Theory. Determining whether a general graph is Hamiltonian, path-Hamiltonian or neither is, therefore, at this stage of the development of graph theory, something of an ad-hoc process. Many sufficient conditions for Hamiltonicity are applicable only to 'dense' graphs with a high edges/vertices ratio and are therefore particularly inappropriate for the very 'sparse' graphs (with a low edges/vertices ratio) which we are using here to represent conjugated systems of chemical interest. In Appendix C we therefore propose and prove some necessary conditions for a sparse graph to be Hamiltonian, based on its connectivity. This is of considerable use for, just as a sufficient condition can assure us that a given graph G is Hamiltonian, a necessary condition can guarantee that G is not Hamiltonian. When the graph whose Hamiltonicity is being investigated is not Hamiltonian, a necessary condition is thus somewhat more appropriate (see Appendix C).

It turns out, in fact, that conjugated systems within which no path-Hamiltonian spanning-trees can be devised seem to be rather uncommon; one molecular graph which is, however, non path-Hamiltonian is that possessed by the ten-ring system decacyclene (Figure 6.2a). Figure 6.2b shows a spanning tree which contains three branches and Figure 6.2c shows a tree containing just a single branch. Trial and error (or application of the discussion and ideas presented in Appendix C) should convince the reader that it is evidently not possible to devise a spanning tree for this molecular graph which contains no branches at all (i.e. which is path-Hamiltonian); to such a system, therefore, only the Gayoso-Boucekkine transformation^{165a} can be applied.

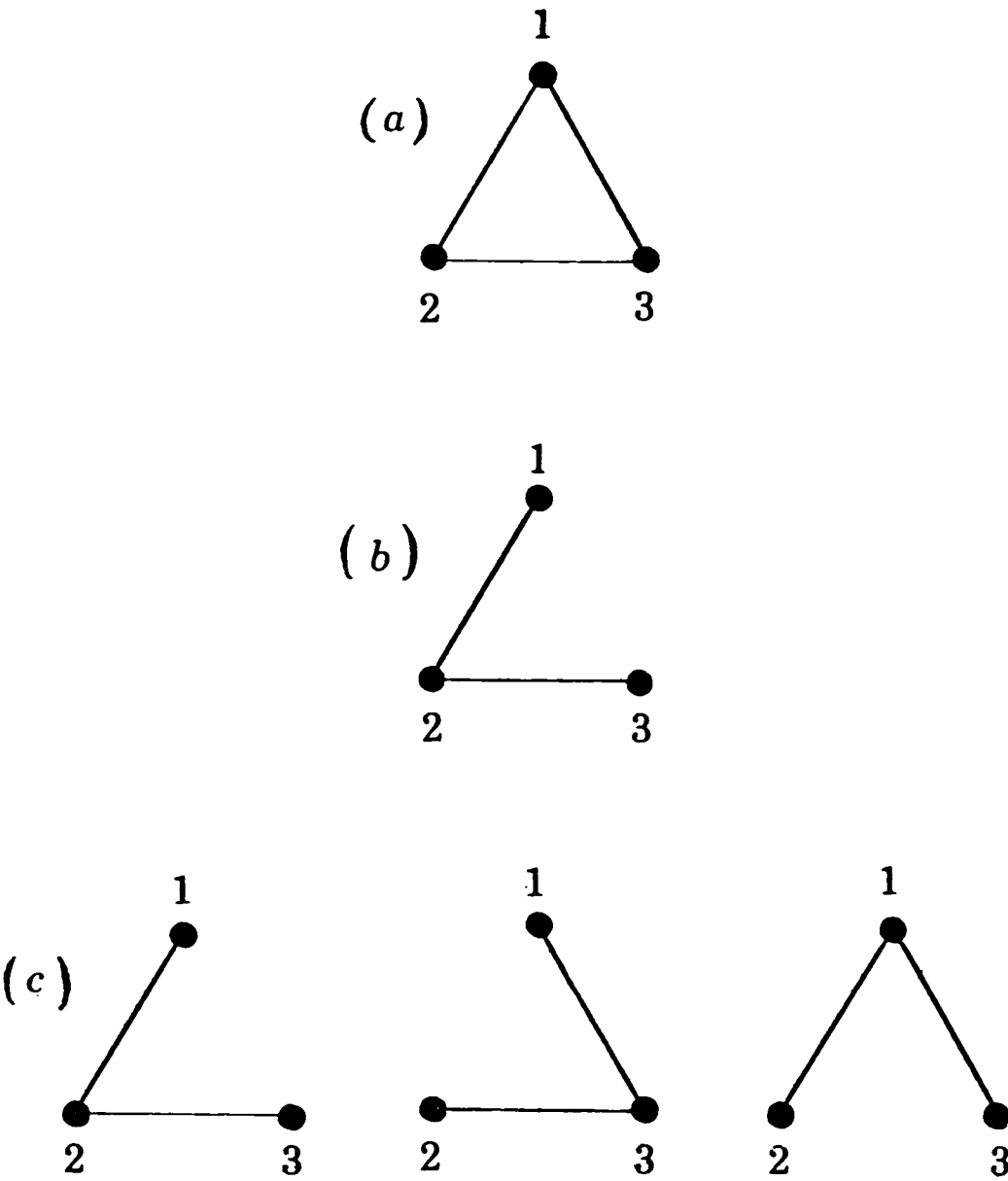
(v) An Upper Bound for the Number of Chemically Distinct
Spanning-Trees in a Given Molecular-Graph: The Matrix-Tree Theorem

The preceding discussion may prompt the question - how many different spanning-trees (whether branched or not) can be constructed within any given molecular graph? This question can be partially answered by noting, first, that there are a number of distinct ways in which the N vertices of a simple connected graph G can be labelled[†]; when any one of these different labelling-schemes has been arbitrarily selected, the number of distinct spanning-trees based on it can then be ascertained by means of an ingenious theorem known as the Matrix-Tree Theorem (see ref. 305, on p.152, for a proof). This theorem is often erroneously attributed to Kirchhoff³³⁷ (1847), although in fact it is due to Tutte.³³⁸

Firstly, an $N \times N$ matrix, $\mathbb{T}$, is constructed, similar, in many respects, to the adjacency matrix, except that T_{ij} ($i \neq j$) is minus 1 if the vertex labelled i , on the particular scheme adopted, is joined to vertex j , and is zero otherwise; and the diagonal element, T_{ii} , is not zero, as in the adjacency matrix, but is $\rho(i)$, where $\rho(i)$ is the degree of vertex i . (Note that since there will be as many -1 terms in any given row, r , of this matrix, as there are edges joined to vertex r , it is immediately evident that the sum of elements along any one row is zero; thus, the columns (and also, therefore, the rows) of $\mathbb{T}$ are not linearly independent, and so $\mathbb{T}$ is singular). The matrix $\mathbb{T}$ then has the remarkable property that all N^2 cofactors of it are identical, and the Matrix-Tree Theorem asserts simply that this unique

[†] The actual number of such distinct ways is $N!/g$, where g is the order of the automorphism group of G ³⁰⁷. In this context, an automorphism, ϕ , is defined as a one-to-one mapping of the vertex set of G onto itself, with the property that $\phi(u)$ is joined to $\phi(v)$ if and only if u is joined to v ; it can then be shown that the automorphisms of a graph G form a group under composition.

FIGURE 6.3



Graphs Illustrating Application of the Matrix-Tree
Theorem (See Page 180)

cofactor is numerically equal to the number of distinct spanning-trees of G.

The theorem is well illustrated by the graphs shown in Figures 6.3a and 6.3b; for the graph of circuit rank 1 shown in Figure 6.3a, the appropriate form for the matrix $\overline{\mathbf{U}}$, with the labelling scheme adopted in this Figure, is:

$$\begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix}$$

of which all the cofactors (the reader may verify) are 3 — corresponding to the three distinct spanning-trees for this graph, shown in Figure 6.3c.

The spanning tree of a simple, connected graph of circuit rank zero is, of course, (trivially) the graph itself, and so there evidently is only one distinct spanning-tree for such a graph; accordingly, the matrix $\overline{\mathbf{U}}$ for the graph of Figure 6.3b, labelled as in that Figure, is

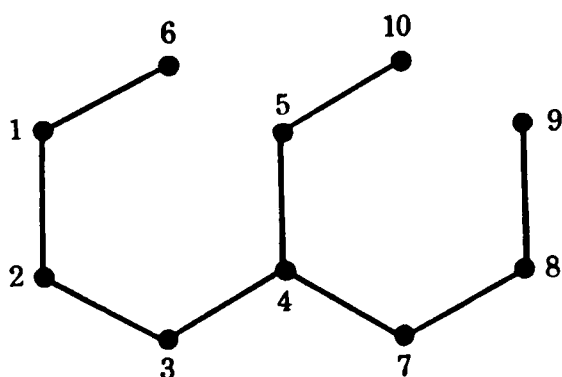
$$\begin{pmatrix} 1 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 1 \end{pmatrix}$$

and all its cofactors are 1, this being the number of spanning trees which the Matrix-Tree Theorem correctly predicts a non-circuit graph to have.

It is to be noted, however, that by 'distinct' spanning-trees the Matrix-Tree Theorem refers to those which are distinct within the labelling scheme adopted, and no concessions are made to what we might intuitively regard as 'chemical equivalence' of edges or vertices, when a molecular graph is depicted with due regard to the spatial, symmetry, geometric, and other requirements of a chemical structural-formula (none of which, of course, features at all in a graph-theoretical conceptual-scheme). Thus, the spanning tree shown in Figure 6.4 for the naphthalene molecular-graph might

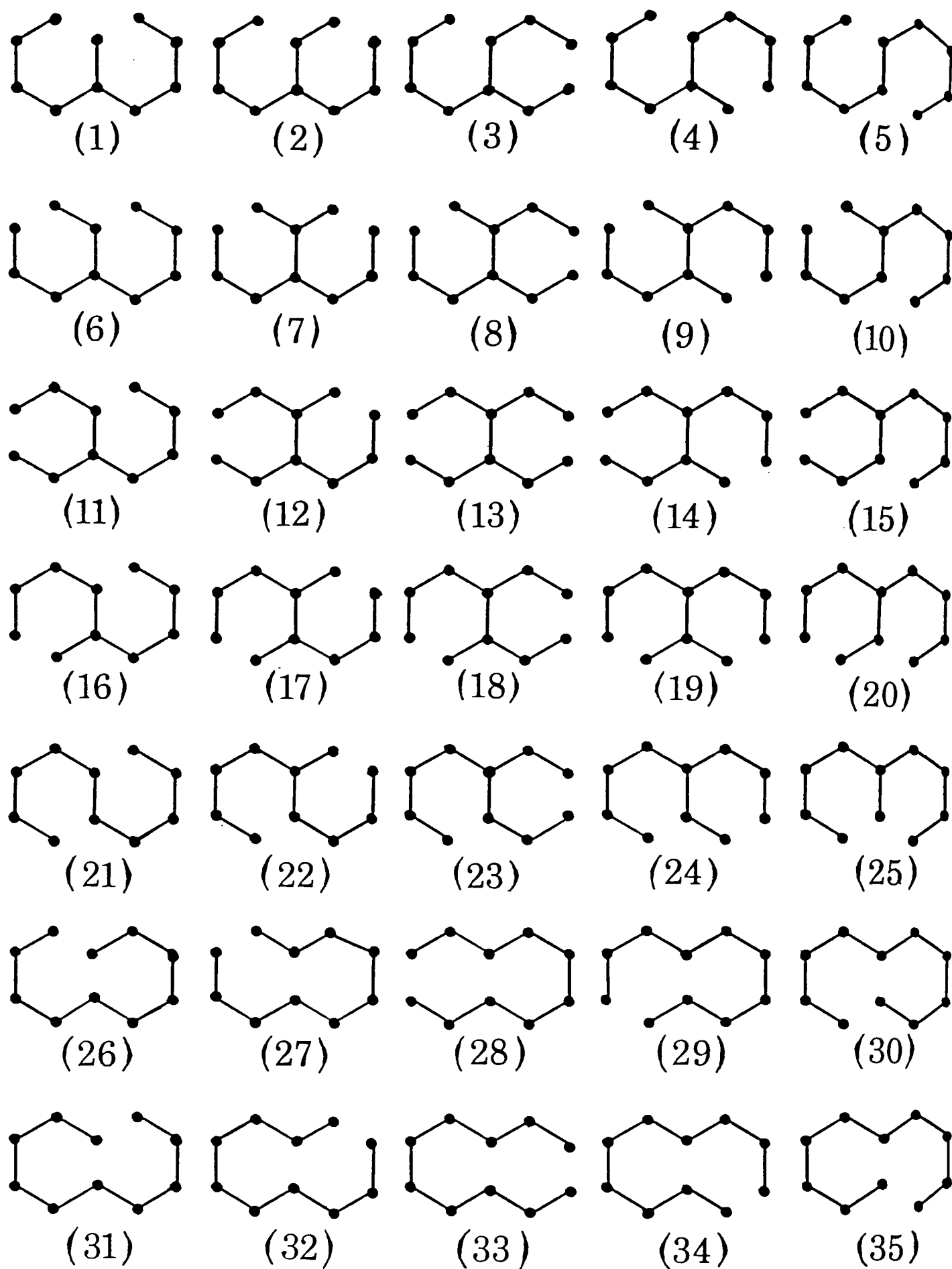
be considered to be 'chemically equivalent' to the one illustrated in Figure 6.1c (since both have been formed by deleting 'chemically equivalent' bonds from the original, complete molecular-graph of naphthalene); however, for the purposes of the Matrix-Tree Theorem, Figures 6.1c and 6.4 would be counted as two different, distinct trees. It is for this reason that the Matrix-Tree Theorem gives only an upper bound for the number of what we might heuristically call 'chemically distinct' spanning-trees in any given molecular-graph. For example, in the case of the benzene molecular-graph, there are evidently six distinct spanning-trees, on the Matrix-Tree Theorem's criteria (since any one of the six distinctly labelled edges can be deleted to form a spanning tree), but there is clearly only one 'chemically distinct' spanning-tree. The naphthalene molecular-graph, on the other hand, has 35 graph-theoretically distinct spanning-trees, according to the Matrix-Tree

FIGURE 6.4



A Spanning Tree of the Naphthalene
Molecular-Graph

FIGURE 6.5



The 35 Graph-Theoretically Distinct Spanning-Trees of the Naphthalene
Molecular-Graph

Theorem (all are illustrated in Figure 6.5), of which twelve (those labelled 1,2,3,4,5,7,8,9,13,26,27 and 28) are 'chemically' distinct. Of these twelve, six (Nos. 2,3,4,8,26 and 27) are 'four-fold degenerate' (i.e. occur four times in the scheme shown in Figure 6.5), five (Nos. 1,5,7,9 and 28) are doubly degenerate, and one (that labelled 13 in Figure 6.5), is unique. Twelve of the graph-theoretically different spanning-trees shown in Figure 6.5 represent Hamiltonian paths within the naphthalene molecular-graph; four of these (Nos. 5,26,27 and 28) are 'chemically' distinct spanning-paths.

(vi) Pauling's Classical "Ring-Current" Theory

It is convenient, at this stage, to consider what relevance the present discussion may have for the entirely classical treatment of the magnetic susceptibilities of polycyclic hydrocarbons proposed in Pauling's 1936 paper¹ (which was the first to introduce the concept of "ring currents" per se, and to indicate a quantitative method for calculating their relative sizes — see §1.3(iii)). Pauling's unashamedly classical approach makes use, in their entirety, of Kirchhoff's laws for current networks and it might therefore be thought to encompass topological features very similar to those inherent in the completely quantum-mechanical formalism which has been our exclusive concern in this chapter, until now. For, naturally, whether the molecular graphs of circuit rank ≥ 1 which we are discussing are Hamiltonian, path-Hamiltonian, or non path-Hamiltonian is a property which remains extant, and is independent of, whatever type of magnetic theory — classical or quantum-mechanical — we care to apply to the molecules which such graphs are

considered to represent^{*}. However, whether or not any given molecular-graph is path-Hamiltonian does not have the same repercussions in a classical calculation of the type described by Pauling, as it does in the quantum-mechanical formalism being considered here; this is so, since, in the former approach, there is, of course, nothing in any way corresponding to the basis orbitals of MO-theory to which unitary transformations such as are discussed in §6.3(ii) and (iii) may be applied. (To this extent, therefore, such unitary transformations, and the dependence of their actual form on the path-Hamiltonian/non-path-Hamiltonian nature of the molecular graph in question, may not improperly be considered as artifacts, by means of which, in the McWeeny approach, the concept of a "ring current" is introduced. It certainly is not necessary to invoke such unitary transformations in order to arrive at the (entirely equivalent) idea of 'bond currents' in polycyclic molecules, via the McWeeny formalism (cf. equation (4.4) of ref. 132 and equations (3.21) and (3.25) of Chapter III), nor to calculate magnetic susceptibilities or chemical shifts¹⁴¹ by this method.) Neither is there any equivalent, in Pauling's classical method, of the quantum-mechanical theory's use of quantities derived from the eigenvectors and eigenvalues of the adjacency matrix of the molecular graph in question in order to calculate the relative magnitudes of the currents in the various constituent-rings of the corresponding polycyclic-system (as is described in §6.4 and in Appendix D.)

* And, indeed, it was in the course of his classic investigations on current networks that Kirchhoff³³⁷ implicitly arrived at the fore-runner of the Matrix-Tree Theorem^{305,338} concerning the number of ways in which a given network can be depleted of its n fundamental circuits, by the successive (and judicious) removal of n appropriate 'arms' of the network. For a much deeper, and more thorough, account of the graph-theoretical aspects of current networks, the reader is referred to refs. 339 and 340.

6.4 Numerical Calculations

(i) A General Formula

In §3.6, from considerations based on the London-McWeeny formalism, we presented an explicit expression (equation (3.33)) for a quantity, J_i , proportional to the "ring-current" intensity in the i^{th} ring of any arbitrary, polycyclic system. Though in outward appearances very different, this is exactly equivalent to another explicit formula devised earlier by Pople¹³¹; the author's version, however, is used here for its origins in the graph-theoretical formalism we have just outlined are more evident. By virtue of the Gayoso-Boucekkine^{165a} transformation, application of the formula can be based on any spanning tree of the molecular graph in question, branched or not. A simplified version of this (in which it is assumed that all resonance integrals, β , between pairs of bonded atoms are the same[†]) is the following:

$$J_i = \sum_{(\mu)} \left[P_{(\mu)} + \beta \bar{\pi}_{(\mu)(\mu)} \right] \mathcal{S}_{(\mu)} \mathcal{L}_{(\mu)}^i + \sum_{(\mu)} \sum_{\substack{(\nu) \\ (\mu < \nu)}} \beta \bar{\pi}_{(\mu)(\nu)} \left[\mathcal{S}_{(\mu)} \mathcal{L}_{(\nu)}^i + \mathcal{L}_{(\mu)}^i \mathcal{S}_{(\nu)} \right] \quad (6.15)$$

In equation (6.15), the $P_{(\omega)}$ terms are the Coulson bond-orders of the various ('circuit-completing') bonds (edges) of the original molecular-graph which must be added to the chosen spanning-tree of the molecular graph, in order to reconstitute its fundamental system of circuits, and $\bar{\pi}_{(\omega)(\chi)}$ is what McWeeny defined as the mutual (or 'self', if $\omega = \chi$) imaginary bond-bond

[†] 'Refinements' such as variation of resonance integrals might be important chemically, in any given calculation (and will certainly be necessary when heterocyclic systems are being dealt with)^{180,341}, but they are not relevant from a topological point of view (which is what we are concerned with here) and would only serve to complicate the discussion — hence, we omit them. For the more-general form of equation (6.15), see equation (3.33).

polarisability of two such bonds. Both $P_{(\omega)}$ and $\bar{\pi}_{(\omega)}(\chi)$ may be said to be topological indices in that, once given the Aufbau Principle³⁰³, they are calculable solely from the eigenvectors and eigenvalues of the relevant molecular-graph (see Appendix D); $\mathcal{S}_{(\omega)}$ is the algebraic area (expressed as a ratio to the area, S , of a standard benzene-hexagon) of the circuit completed when the ω^{th} - edge (only) is inserted into the spanning tree on which the calculation is being based; and $\mathcal{L}_{(\omega)}^i$ is a topological quantity which is non-zero only if the circuit which the insertion of edge ω creates contains the ring i if it does, then $\mathcal{L}_{(\omega)}^i = +1$ if the ω^{th} circuit-completing bond is defined in the anti-clockwise sense around the circuit it completes, and -1 if this bond is defined in the clockwise sense around that circuit.[†]

(ii) Application to Naphthalene

(a) Spanning tree (a) (Figure 6.1): Calling the circuits which edges $6 \rightarrow 1$ and $10 \rightarrow 5$ complete I and II, respectively, and the 'left-hand' and 'right-hand' rings A and B, we observe that $\mathcal{L}_{(I)}^A = 1, \mathcal{L}_{(I)}^B = 0$, $\mathcal{L}_{(II)}^A = 0$ and $\mathcal{L}_{(II)}^B = -1$. Insertion of these values, together with the bond orders, polarisabilities and circuit areas given by McWeeny,¹³² into equation (6.15), correctly gives rise to his value of 0.1214 for J_A and J_B .

(b) Spanning tree (b) (Figure 6.1): Here, the edges completing circuits I and II are $6 \rightarrow 1$ and $10 \rightarrow 1$, respectively; and $\mathcal{L}_{(I)}^A = \mathcal{L}_{(I)}^B = 0, \mathcal{L}_{(II)}^A = 1, \mathcal{L}_{(II)}^B = 1$; these, together with McWeeny's data for this spanning tree, again give 0.1214 for J_i in the two equivalent rings.

[†] The quantity J_i having been calculated from equation (6.15), the actual "ring-current" intensity in the i^{th} ring is then

$$8\pi^2 \beta \left[\frac{e}{h} \right]^2 S_B J_i$$

(c) Spanning tree (c) (Figure 6.1): Since this calculation is based on a branched spanning-tree, we give more details of it. First, using the same nomenclature as for case (a), we find $\mathcal{S}_{(I)} = 1$, $\mathcal{S}_{(II)} = 1$, $\mathcal{L}_{(I)}^A = 1$, $\mathcal{L}_{(I)}^B = 0$, $\mathcal{L}_{(II)}^A = 0$, $\mathcal{L}_{(II)}^B = 1$;

$$P_{(I)} = 0.72456, P_{(II)} = 0.55470;$$

$$\beta \bar{\pi}_{(I)(I)} = -0.63587, \quad \beta \bar{\pi}_{(II)(II)} = -0.46601,$$

$$\beta \bar{\pi}_{(I)(II)} (= \beta \bar{\pi}_{(II)(I)}) = 0.03271.$$

When these quantities are substituted into equation (6.15), 0.1214 is again obtained for J_A and J_B .

(d) Finally, we consider tree (d) (Figure 6.1), (again a branched tree). Denoting, this time, the circuits completed by $6 \rightarrow 1$ and $10 \rightarrow 6$ by I and II, respectively, we see immediately that $\mathcal{L}_{(\omega)}^i$ and $\mathcal{S}_{(\omega)}$ terms are precisely as for case (c), above, but that (by application of the formulae presented in Appendix D) $P_{(I)}$ is now 0.55470 ($=P_{(II)}$), $\beta \bar{\pi}_{(I)(I)} = \beta \bar{\pi}_{(II)(II)} = -0.46601$, and $\beta \bar{\pi}_{(I)(II)} = 0.03271$. The reader may then easily confirm that these once more give rise, via equation (6.15), to 0.12140 for the J_i 's. Since J_{Benzene} in these units is $\frac{1}{9}$, the intensity of the naphthalene "ring-current", relative to that in benzene, is 1.093 — the value also obtained¹²⁰ by application of Pople's¹³¹ formula.

(iii) Application to Decacyclene

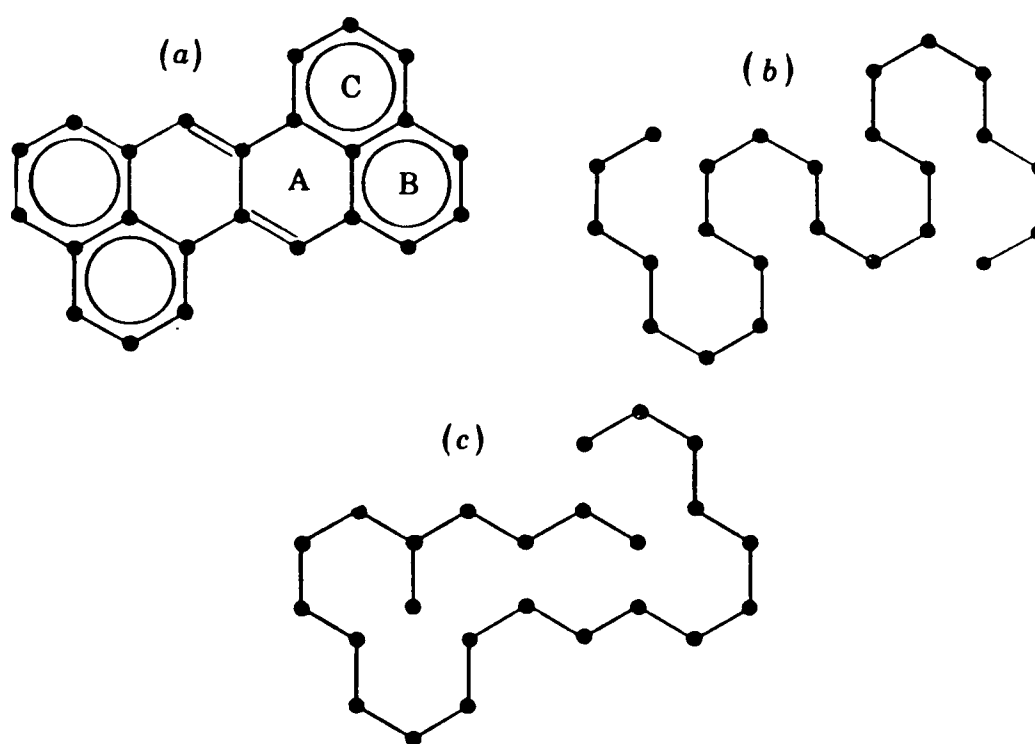
The intermediate details of a calculation on this 10-ring system with its associated non-path-Hamiltonian molecular-graph are too tedious to reproduce here; however, application of equation (6.15) to either of the spanning trees illustrated in Figure 6.2 (or indeed to any other such trees which might be devised within the decacyclene molecular-graph), gives rise to "ring-current" intensities (expressed as a ratio to the benzene "ring-

current") of 0.965 for the outer hexagonal-rings, 0.610 for the central hexagonal-ring, and $-0.014^\dagger$ for the pentagonal rings, leading (via, for example, equations (3.17)-(3.20) of Chapter III) to an overall 'London' diamagnetic-anisotropy for this molecule (again expressed as a ratio to that calculated for benzene) of 6.36 — very low indeed for a 10-ring system.

(iv) Application to Zethrene

As an example of the application of equation (6.15) to a large polycyclic-hydrocarbon with a path-Hamiltonian molecular-graph, we consider zethrene

FIGURE 6.6



Zethrene and Two of its Spanning Trees

$\dagger$ That is to say, marginally paramagnetic, if any physical significance which a calculation at this level of approximation may have is to be interpreted literally. Furthermore, this calculation was based on the assumption that the areas of six-membered and five-membered rings are in the ratio $6 \cot(\pi/6) : 5 \cot(\pi/5)$ (i.e. ca. 1.0: 0.66) and it is possible that basing the calculation on a slightly different molecular-geometry could well 'tip the balance' and result in the prediction of a marginally diamagnetic "ring-current" for this ring; this speculation, however, has not been further investigated here. The whole question of paramagnetic "ring-currents" is fully discussed in Chapter VIII.

(Figure 6.6a), an interesting molecule categorised by Clar³⁴² as being in that class of polycyclic hydrocarbons which have "formally fixed double-bonds"; in the central rings, A, of this molecule (Figure 6.6a) the bonds indicated never appear other than as double bonds in any of the several Kekulé-structures which can be devised for the molecule as a whole[†]. It is, therefore, of some interest to investigate whether, in view of this peculiarity, significantly different "ring-currents" are predicted from those calculated for other hexacyclic, benzenoid hydrocarbons (a point which is examined in detail in Chapter VII). Figure 6.6b shows a Hamiltonian path, and Figure 6.6c a branched spanning-tree, of the zethrene molecular-graph. Application of equation (6.15), and the relevant formulae for the polarisabilities, to these spanning trees, gives calculated "ring-current" intensities, relative to benzene, of 0.365 for the central rings A, and 0.865 and 0.922 for the rings labelled B and C, respectively, in Figure 6.6a. Not only is such a low "ring-current" in the central rings consistent with heuristic and intuitive ideas about "bond fixation" (cf. the calculations on perylene and peropyrene reported in Chapter VII), but it gives rise to the expectation¹⁴¹ of an unusually high-field shift, in an ¹H NMR- experiment, for the two chemically equivalent protons attached to the rings A (as is, indeed, confirmed experimentally^{347,348}) as well as to the prediction of a diamagnetic anisotropy, relative to benzene, of only 4.30 — again, quite low for a system of this size; (for example, the linear, six-ring benzenoid-hydrocarbon hexacene is calculated¹⁴¹ to have a 'London' diamagnetic-anisotropy of 7.38, expressed as a ratio to the corresponding value calculated for benzene).

[†] Note that the Valence-Bond Resonance-Theory prescription for drawing the various unexcited ('Kekulé') structures for a conjugated system indicates that this activity can also be regarded as a purely graph-theoretical exercise³⁴³⁻³⁴⁶. This interesting aspect is further explored in §7.5.

6.5 Conclusions

In this chapter, we have attempted to highlight some of the graph-theoretical aspects of "ring-current" calculations on conjugated molecules. In so-doing, we have drawn attention to the fact that the various unitary-transformations which have been suggested in the Literature do correctly give rise to the "ring-current" concept for systems whose molecular graphs are path-Hamiltonian (whether the calculations for such molecules are based on a spanning tree which is 'unbranched' — i.e. is a Hamiltonian path — or is 'branched'), as well as for those systems (such as decacyclene) possessed of molecular graphs which are apparently non path-Hamiltonian — as evidently must be the case if there is to be any possibility whatever of the "ring-current" model's having a physical basis. We have also emphasised that equation (6.15) is perfectly general within the simplest HMO-approximation and applies equally to all such cases.

It should however be noted that although, in the context of the simple Hückel-London scheme, the MO-quantities used in the calculation of the "ring-current" intensities (the Coulson bond-orders and the imaginary bond-bond polarisabilities) are calculated solely* from the eigenvalues and eigenvectors of the adjacency matrix of the molecular graph in question (see Appendix D), the same is not true of the "ring-current" intensities themselves; for, as examination of equation (6.15) confirms, in addition to depending on these topological MO-indices $P_{(\omega)}$ and $\bar{\pi}_{(\omega)}(\chi)$ (and the $\ell_{(\omega)}^i$ factors, which are also topological), the J_i -terms also depend on the geometry of the conjugated system, via the 'circuit-area' terms, $\mathcal{S}_{(\omega)}$.

* This statement is only strictly true once the Aufbau Principle has been assumed. This point has been developed in a subsequent article by the present author and Rouvray³⁰³, and is further alluded to in §7.7.

Therefore, although, as we have tried to indicate, there is much graph theory implicit in the concept and calculation of π -electron "ring-currents", it should be borne in mind that, in the final analysis, the "ring-current" index itself is manifestly not a completely topological quantity — even when a purely topological wave-function (such as the simple Hückel one) has been used to calculate it.

CHAPTER VII

RATIONALISATION OF RELATIVE "RING-CURRENT" SIZES IN POLYCYCLIC, CONJUGATED HYDROCARBONS

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CHAPTER VII

RATIONALISATION OF RELATIVE "RING-CURRENT"
SIZES IN POLYCYCLIC, CONJUGATED HYDROCARBONS*7.1 Introduction

Although McWeeny's approach¹³² has been applied by a large number of authors^{132,114,116,155,173,163,30,111,140,141,38b,162,348}, over the last 15-20 years, to calculate "ring currents" in a wide range of hydrocarbons, and the equivalent method of Pople¹³¹ has also received some attention^{120,82}, little consideration appears to have been given to the relative sizes of the "ring-current" intensities which arise from these calculations. If the (diamagnetic) "ring-current" in benzene is taken to be unity, the smallest "ring-current" so far reported for a condensed, benzenoid hydrocarbon is 0.236 (in benzo [b] perylene, compound (XXI) of ref. 141), while in the 19-ring benzenoid-hydrocarbon dodecabenzocoronene Maddox and McWeeny¹¹⁴ found a diamagnetic "ring-current" intensity as large as 2.44. When non-alternant (or otherwise

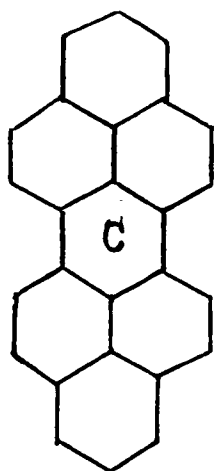
* Some of the numerical calculations reported in this chapter have been published. The full references are:

- (a) R.B. MALLION, " π -Electron 'Ring-Currents' in Fluoranthene and Related Molecules", J.Molec. Spectroscopy, 1970, Vol. 35, pp.491-493.
- (b) R.B. MALLION, "Calculation of the π -Electron 'Ring-Current' Properties of Some Carcinogenic, Heptacyclic, Condensed, Benzenoid Hydrocarbons", J. Medicinal Chem., 1971, Vol. 14, pp.824-826.
- (c) R.B. MALLION, "Approximate, π -Electron 'Ring-Current' Intensities in Some Sulphur-Heterocyclic Analogues of Fluoranthene", J.Chem.Soc. Perkin Transactions, 1973, pp.235-237.
- (d) R.B. MALLION, "Sur les Courants de Cycle d'Électrons π de Quelques Hydrocarbures Polycycliques et Cancérogènes et de Leurs Isostères Azotés Correspondants", Biochimie, 1974, Vol.56, pp.187-188.

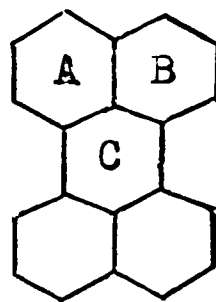
Some of the ideas in this chapter were arrived at in collaboration with Mr. C.W. Haigh (University College, Swansea, University of Wales), and are included here by his kind permission. I should also like to acknowledge fruitful discussion and correspondence on this subject-matter with the late Professor C.A. Coulson.

non-benzenoid) conjugated-hydrocarbons are considered, smaller diamagnetic, or even large paramagnetic, "ring-currents" may be encountered^{19,20,30,82,162,348} as they were, for example, in §6.4(iii), and will be in the present chapter and in Chapter VIII.

Within the domain of the condensed, benzenoid hydrocarbons, it has been observed empirically^{116,141} that the more condensed a given ring is, the smaller the "ring-current" it appears to bear. A dramatic exception to this rule, however, is the central ring (C) in peropyrene (XVII) which has an associated "ring-current" intensity of 1.446* — over six times that^{116a,140} (0.239) in the formally analogous central-ring (C) in perylene (XII) which, locally, is similarly condensed with four surrounding rings. Perturbations brought about by condensation of



(XVII)



(XII)

* "Ring-current" intensities quoted in this chapter without reference to Literature sources have all been calculated, via programs prepared for the Oxford-University KDF-9 and ICL-1906A computers, by use of 1) equations (3.33) and (6.15) and equations (D1)-(D5) of Appendix D, and 2) the assumptions that all C-C bond-lengths have the standard benzene-value ($1.397\text{\AA}$), and that the areas of five-, six-, and seven-membered rings are in the ratio $5 \cot(\pi/5) : 6 \cot(\pi/6) : 7 \cot(\pi/7)$. They are always expressed as a ratio to the "ring-current" intensity calculated, by the same method, for benzene.

additional rings in one region of a large, condensed, benzenoid hydrocarbon may often have only a second-order effect on the "ring-current" intensities in rings distant from the site of the perturbation — though, evidently, this is by no means always the case, as the above comparison between (XVII) and (XII) indicates.

It is these sorts of observations, amongst others, which we aim to rationalise in this chapter, by appeal to a well-known argument in perturbation theory³⁴⁹, and by invoking some topological considerations. We first examine, in more detail than we did in §1.4(i)(i), §6.4 and Appendix D, some properties of imaginary bond-bond polarisabilities and their relevance in "ring-current" calculations.

7.2 Preliminaries on Imaginary Bond-Bond Polarisabilities

(i) Polarisabilities and "Bond Currents"

$\bar{\pi}_{(tu)(wv)}$, the mutual, imaginary, bond-bond polarisability between two bonds $t \rightarrow u$ and $w \rightarrow v$ of the conjugated system, is defined (see equations (D1) and (D2)):

$$\bar{\pi}_{(tu)(wv)} = \pi_{tu,wv} - \pi_{tu,vw} + \pi_{ut,vw} - \pi_{ut,wv} \quad (7.1)$$

in which, for a hydrocarbon with N carbon-atoms and M doubly-occupied orbitals,

$$\beta\pi_{tu,wv} = 2 \sum_{I=1}^M \sum_{J=M+1}^N \frac{c_{tI} c_{uJ} c_{wJ} c_{vI}}{x_I - x_J} \quad (7.2)$$

where $E_I = \alpha + x_I \beta$ is the energy of the I th HMO, $\{c_{tI}\}$ ($t = 1, 2, \dots, N$). For even, alternant hydrocarbons, these expansions simplify, as shown in Appendix D (equations (D3) - (D5)). $\bar{\pi}_{(tu)(wv)}$ is thus seen to be closely related to the real, mutual, imaginary bond-bond polarisability, $\pi_{(tu)(wv)}$, earlier proposed by Coulson and Longuet-Higgins.¹³⁹ In terms of the $\pi_{tu,wv}$ - quantities defined in equation (7.2), the latter is

$$\pi_{(tu)(wv)} = \pi_{tu,wv} + \pi_{tu,vw} + \pi_{ut,vw} + \pi_{ut,wv} \quad (7.3)$$

McWeeny stated¹³² that there are more relations between the imaginary polarisabilities than there are amongst the real ones. By using arguments which rely on the origin independence of bond currents, we may express these relations in general form, as follows.

The secondary field at the origin is given by equation (1.93), with σ_1 and σ_2 of that equation defined by equation (1.92). (Note that we are here dealing with McWeeny's formulation before application of his unitary transformation, much discussed in §6.3). By writing the sum of σ_1 and σ_2 in the form

$$\sigma_1 + \sigma_2 = \sum_{\substack{\text{bonds} \\ (tu)}} J_{tu}^{\text{bond}} s_{tu} k_{tu} \quad (7.4)$$

we may identify the term

$$J_{tu}^{\text{bond}} = (p_{tu} + \beta \bar{\pi}_{(tu)(tu)}) s_{tu} + \sum_{\substack{(wv) \\ \neq (tu)}}' \beta \bar{\pi}_{(tu)(wv)} s_{wv} \quad (7.5)$$

as the "bond current" associated with the bond $t \rightarrow u$. (See equation (3.21)). This quantity, made use of in §3.5, is analogous to the "bond-current densities" discussed in certain SCF-treatments based on the current-density operator (see §1.4(ii)(c)) and it is, therefore, origin independent. This property is, at first sight, surprising, since J_{tu}^{bond} is seen to depend explicitly on the area-quantities s_{wv} ; however, it is just this origin dependence of the s_{wv} -terms which necessitates relationships amongst the polarisabilities and bond orders, if J_{tu}^{bond} is finally to be invariant to a change of origin.

(ii) Monocyclic Case (Benzene)

In the monocyclic case,

$$\sum_{\substack{\text{all bonds} \\ (tu)}} s_{tu} = \text{ring area (origin independent)}$$

— see §1.4(i)(f), equation (1.56); this (hexagonal) ring-area is here taken to be unity. This means that the coefficient of each area-term in equation (7.5) must be identical, and thus, for all bonds (tu),

$$P_{tu} + \beta \bar{\pi}_{(tu)(tu)} = J \quad (7.6)$$

and, for all pairs of distinct bonds (tu) and (wv),

$$\beta \bar{\pi}_{(tu)(wv)} = J \quad (7.7)^*$$

* Explicitly, the right-hand-side of (7.7) is really $J \times S$, — where S is the area of the monocycle — with $S = 1$.

where J is now the (unique) "ring-current". (In the monocyclic case, since no bonds are shared with other rings, the "bond current" associated with each bond is identical to the "ring current" which characterises the ring as a whole.)

For a six-membered ring with no symmetry these considerations imply that 21 distinct quantities have identical values.

(iii) Bicyclic Case (Naphthalene)

Let $i \rightarrow j$ be an unshared bond in ring 1.

Then, from equation (7.5),

$$\begin{aligned}
 J_{ij}^{\text{bond}} = & (P_{ij} + \beta \bar{\pi}(ij)(ij)) s_{ij} + \sum_{\substack{(kl) \\ \neq (ij) \\ \text{(ring 1, unshared bonds)}}} \beta \bar{\pi}(ij)(kl) s_{kl} \\
 & + \sum_{(mn)} (\beta \bar{\pi}(ij)(mn) s_{mn}) + \beta \bar{\pi}(ij)(wv) s_{wv} \\
 & \text{(ring 2, unshared bonds)}
 \end{aligned} \tag{7.8}$$

where $w \rightarrow v$ is the bond shared between rings 1 and 2.

Now,

$$\sum_{(kl)} s_{kl} = \sum_{(mn)} s_{mn} = \text{Constant } (= 1) \tag{7.9}$$

(ring 1, shared and unshared bonds) (ring 2, shared and unshared bonds)

For J_{ij}^{bond} to be origin independent, therefore, it follows that all

coefficients of ring-1 areas must be equal, and that the coefficients of ring-2 areas similarly are all equal. Hence (remembering that $i \rightarrow j$ is any unshared bond in ring 1)

$$P_{ij} + \beta \bar{\pi}_{(ij)(ij)} = J^{1,1} \quad (\text{say}) \quad (7.10)$$

For all other unshared bonds in ring 1 $(kl) (\neq (ij))$,

$$\beta \bar{\pi}_{(ij)(kl)} = J^{1,1} \quad (7.11)$$

Likewise, for all unshared bonds, (mn) , in ring 2:

$$\beta \bar{\pi}_{(ij)(mn)} = J^{1,2} \quad (7.12)$$

For the sole, shared bond, (wv) , since $\bar{\pi}_{(rs)(tu)} = -\bar{\pi}_{(rs)(ut)}$

we must have

$$\beta \bar{\pi}_{(ij)(wv)} = J^{1,1} - J^{1,2} \quad (7.13)$$

Finally, since $i \rightarrow j$ is an unshared bond,

$$\begin{aligned} J_1^{\text{ring}} &= J_{ij}^{\text{bond}} \\ &= J^{1,1} + J^{1,2} \\ &= (\text{say}) \beta \bar{\pi}_{(12)(23)} + \beta \bar{\pi}_{(12)(56)} \quad , \end{aligned} \quad (7.14)$$

where J_1^{ring} is the "ring-current" intensity which characterises ring 1.

Similar formulae define $J^{2,2}$ and J_2^{ring} . Thus, for an unsymmetrical naphthalene-like molecule we obtain $J^{1,1}$, $J^{1,2}$ and $J^{2,2}$; there are now no less

than 55 distinct quantities which are equal to one of these, or are related to them by simple subtraction!

(iv) Q-Cyclic Case

As will now be shown, the above arguments may be generalised so that, for certain Q-cyclic systems composed of regular hexagons of carbon atoms (qualified later),

$$J_1^{\text{ring}} = \sum_{r=1}^Q J^{1,r} \tag{7.15}$$

Proof: For any unshared bond in ring 1

$$J_{ij}^{\text{bond}} = (P_{ij} + \beta \bar{\pi}(ij)(ij)) s_{ij} + \sum_{\substack{(kl) \\ \neq (ij) \\ \text{(unshared bonds in ring 1)}}} \beta \bar{\pi}(ij)(kl) s_{kl}$$

$$+ \sum_{r=2}^Q \sum_{\substack{\text{completely} \\ \text{unshared bonds} \\ (mn) \text{ in ring } r}} \beta \bar{\pi}(ij)(mn) s_{mn}$$

$$+ \sum_{\substack{\text{Bonds (st)} \\ \text{shared between} \\ \text{ring 1 and other} \\ \text{rings}}} \beta \bar{\pi}(ij)(st) s_{st} + \sum_{\substack{\text{Bonds (uv) shared} \\ \text{between certain} \\ \text{combinations of} \\ \text{rings 2 to Q}}} \beta \bar{\pi}(ij)(uv) s_{uv}$$

Again, all terms of the form $\sum s_{wv}$ taken (in the anticlockwise sense) around a given ring are a constant (assumed here to be unity).*

Then, for the bond $i \rightarrow j$:

$$P_{ij} + \beta \bar{\pi}_{(ij)(ij)} = J^{1,1} \quad (7.17)$$

and, for (ij) and the completely unshared bonds (kl) in ring 1,

$$\beta \bar{\pi}_{(ij)(kl)} = J^{1,1} \quad (7.18)$$

For the completely unshared bonds (mn) in ring r :

$$\beta \bar{\pi}_{(ij)(mn)} = J^{1,r} \quad (7.19)$$

For the bonds, (st) , shared between ring 1 and some (or, possibly, all) other rings, w

$$\beta \bar{\pi}_{(ij)(st)} = J^{1,1} - J^{1,w} \quad (7.20)$$

For the bonds, (uv) , shared between pairs of rings, p and q ($p \neq q \neq 1$),

$$\beta \bar{\pi}_{(ij)(uv)} = (J^{1,p} - J^{1,q}) \quad (7.21)$$

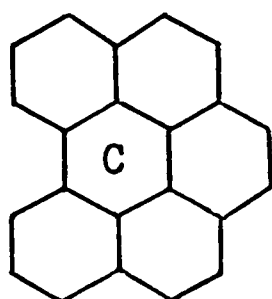
In equation (7.16), since the bond (ij) in ring 1 is an unshared bond,

$$J_{ij}^{\text{bond}} = J_1^{\text{ring}} \quad (7.22)$$

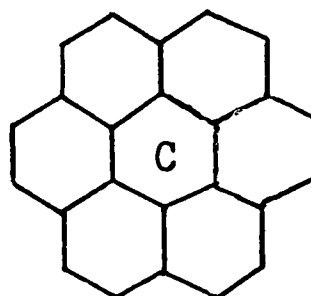
* But see comments in §7.7.

Substitution of equations (7.17) - (7.21) into (7.16) and using the fact that $\sum_{\substack{\text{wv} \\ \text{around ring r}}} s_{\text{wv}} = 1$

for all rings, r , then leads to equation (7.15). It should be noted that this formulation applies only if the ring numbered 1 in the above proof contains at least one unshared bond — i.e. it could be applied to, say, benzoperylene (XVIII) central ring, C , but not (without modification) to the central ring in coronene (XVI).



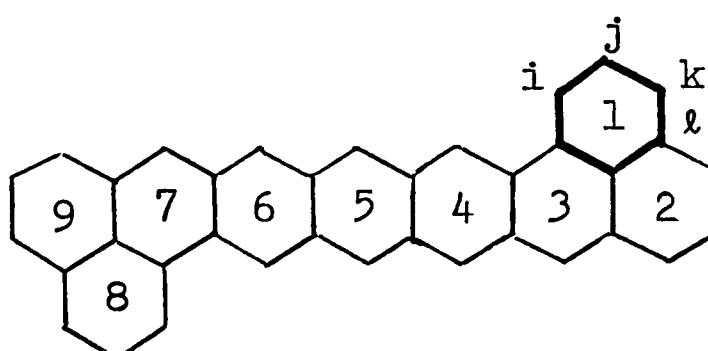
(XVIII)



(XVI)

(v) Numerical
Example

As an example, we consider the ring indicated in nonazethrene (XIX), and focus attention on the bond (ij).



(XIX)

By computation:

$$P_{ij} + \beta\bar{\pi}(ij)(ij) = 0.64069 - 0.56445 = 0.07624$$

and $\beta\bar{\pi}(ij)(kl) = 0.07624$
 $= J^{1,1}$

The other $J^{1,r}$ - terms required are listed in Table 7.1.

TABLE 7.1 Some $J^{1,r}$ -terms for Nonazethrene (XIX)

r	$J^{1,r}$	r	$J^{1,r}$
2	0.01797	6	0.00017
3	0.00303	7	0.00004
4	0.00103	8	0.00001
5	0.00043	9	0.00001

$\sum_{r=1}^9 J^{1,r}$ is thus 0.09893; since $J_{\text{benzene}}^{\text{ring}}$ in these units is $^{132} \frac{1}{9}$, J_1^{ring}

relative to benzene is 0.890. This checks exactly with the value calculated via the full procedure of equation (6.15) — an equation which arises after application of the unitary transformation (see §§ 3.4 and 6.4).

7.3 High and Low "Ring-Currents":
Perturbation-Theory Argument

(i) General Considerations

Examination of the structural formulae of perylene (XII) and peropyrene (XVII) shows immediately that the central links (in ring C) connecting the two naphthalenic moieties in perylene are 'essentially

single' bonds — i.e. no Kekulé structure may be devised for the molecule as a whole in which these bonds are double — while the same is not true of the central links (ring C) in peropyrene. Many years ago, Dewar and Longuet-Higgins³⁴⁹ showed that Pauling bond-order is proportional to HMO-(Coulson) bond-order predicted by perturbation theory (see also ref. 350). As the central bonds in ring C of perylene have zero Pauling- π -bond-order, their (first-order) perturbed Coulson-bond-orders would also be zero — but, again, this is not true for the central links in (XVII). Thus, if one were heuristically to think of 'aromaticity' in terms of first-order stabilisation of energy by ring formation, ring C in peropyrene would be considered 'aromatic' while ring C in perylene would have to be regarded as 'non-aromatic'.

This is, however, not sufficient, for we are concerned here with large and small "ring-currents"; and it is only intuitively likely — and not in any way mathematically obvious — that the two run parallel. In view of the expression

$$J^{1,1} = P_{tu} + \beta \bar{\pi}_{(tu)}(tu),$$

any naïve attempt to relate J^{ring} to P_{tu} is immediately frustrated by examining computed values of these quantities for a given molecule. It is found that the two terms P_{tu} and $\beta \bar{\pi}_{(tu)}(tu)$, making diamagnetic and paramagnetic contributions, respectively, are entirely commensurate in size, and one figure is always lost in cancellation. Therefore, although it does seem that, in general, P_{tu} and $J^{1,1}$ follow the same trends, it would be most hazardous actually to assume this without further, and less-superficial, investigation.

(ii) Perturbation-Theory Argument

We therefore invoke some previous arguments in perturbation theory³⁴⁹ in order to examine the values of imaginary bond-bond polarisabilities

under these circumstances. Two moieties, A and B, are imagined to be brought together, whereupon two 'new' bonds, (tu) and (vw), are formed between them, these bonds then being considered to perturb the two original moieties (see Figure 7.1). For example, if A and B were

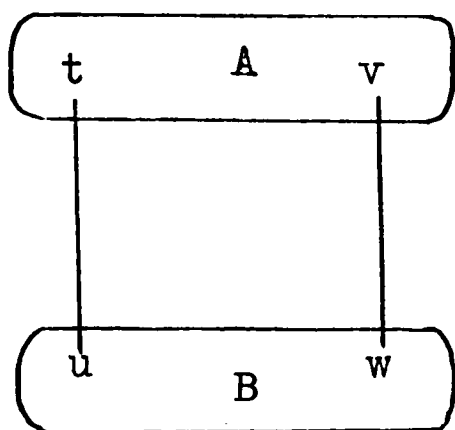


FIGURE 7.1

both 'naphthalenic' fragments, the resulting molecule could be perylene (XII); if they were both 'perinaphthalene-radical' fragments, peropyrene (XVII) could be formed. A and B need not, of course, be identical and, indeed, for the moment, we consider them (in general) to be different (but see §7.4 (ii)). The individual fragments have the following MO-properties:

$$\begin{aligned}
 \text{Fragment A: MO's } \psi_{\mu} &= \sum_r a_{r\mu} \phi_r : \text{Energies } E_{\mu} = \alpha + x_{\mu} \beta \\
 \text{Fragment B: MO's } \psi_{\rho} &= \sum_s b_{s\rho} \phi_s : \text{Energies } E_{\rho} = \alpha + x_{\rho} \beta
 \end{aligned}
 \tag{7.23}$$

With this arrangement, the perturbation process³⁴⁹ leads to

$$\bar{\pi}_{(tu)(vw)} = 2 \left[\sum_{\mu \in A}^{\text{occ}} \sum_{\rho \in B}^{\text{unocc}} - \sum_{\mu \in A}^{\text{unocc}} \sum_{\rho \in B}^{\text{occ}} \right] \left\{ \frac{a_{t\mu} b_{u\rho} b_{w\rho} a_{v\mu}}{E_{\mu} - E_{\rho}} \right\}
 \tag{7.24}$$

We shall now confine attention to the case in which A and B are alternant-hydrocarbon fragments; it then follows²⁴⁹ that $\bar{\pi}$ between any 'new' bond and any 'old' bond (i.e. one already extant in either of the fragments A and B) is zero. Consequently, not only will $\beta\bar{\pi}_{(tu)(wv)}$ yield $J^{1,1}$, but it will also provide the complete J^{ring} (i.e. "ring-current" intensity) for the newly created ring. For reasons which will become clear in §7.4(i), we further restrict ourselves for the moment to those cases in which both A and B are even alternant-fragments. We can then distinguish three possibilities, according to the 'starring' properties¹⁰ of the atoms in A and B.

(a). t,v same parity¹³⁹; u,w same parity By appeal to the Coulson-Rushbrooke theorem¹⁰, we can write (7.24) as (cf. equation (D3), Appendix D)

$$\beta\bar{\pi}_{(tu)(wv)} = 4 \sum_{\mu \in A}^{\text{occ}} \sum_{\rho \in B}^{\text{occ}} \frac{a_{t\mu} b_{u\rho} b_{w\rho} a_{v\mu}}{x_{\mu} + x_{\rho}} \quad (7.25)$$

In order to appreciate the magnitude of this quantity, we use a mean-value approximation, $(\bar{x})$, for the energies, obtaining

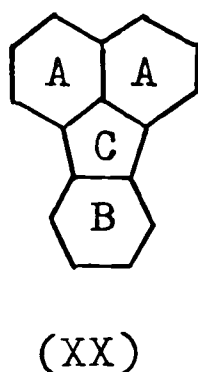
$$\beta\bar{\pi}_{(tu)(wv)} \approx P_{tv}^o P_{uw}^o / (2\bar{x}) \quad (7.26)$$

But, as t,v have the same parity, and u,w have the same parity,

$$P_{tv}^o = P_{uw}^o = 0 \quad (7.27)$$

$\bar{\pi}_{(tu)(wv)}$ is thus the product of two small quantities, and we have therefore shown that $J^{\text{new ring}}$ is small. This is the situation which obtains, for example, in the central ring of perylene (XII).

(b). t,v different parity; u,w same parity. This implies the formation of an odd-membered new ring, such as occurs, for example, (as ring C) when fluoranthene (XX) is formally constructed from naphthalenic (A) and benzenoid (B) fragments. Immediately,



$$\bar{\pi}_{(tu)(wv)} = 0 \quad (7.28)$$

and hence

$$J^{\text{new ring}} = 0 \quad (7.29)$$

$J^{\text{new ring}}$ will not, of course, be precisely zero, for one of our simplifying assumptions in this discussion has been that all rings have the same area as a standard benzene-hexagon, and this is clearly a rather gross approximation* in the case of the five-membered ring in fluoranthene which is only ca.²/₃ of the area of a benzene ring. Nevertheless, the "ring-current" intensities in fluoranthene are in practice calculated** to be as follows:

ring A	ring B	ring C
0.987	0.860	0.050

;

these show that a very small "ring-current" (ca. ¹/₂₀th of the benzene

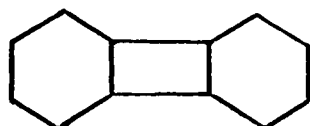
* See, however, the comments in the last paragraph of §7.7.

** See footnote on page 192.

value) is calculated for the five-membered ring of fluoranthene.

(c). t,v different parity; u,w different parity. With this arrangement the exact expression for $\beta\bar{\pi}_{(tu)(wv)}$ is precisely minus the quantity on the ring-hand-side of equation (7.25); the approximate value of it is thus given by minus the quantity on the right-hand-side of equation (7.26) — i.e. $-P_{tv}^0 P_{uw}^0 / (2\bar{x})$. We here distinguish two cases:

α) t,v bonded, u,w bonded. This implies the formation of a four-membered ring. In this arrangement, P_{tv}^0 and P_{uw}^0 are both, in general, large and positive. Therefore $J^{\text{new ring}}$ is large and negative (i.e., paramagnetic). This is the case, for example, with the four-membered ring of biphenylene (XXI) which has¹⁶² a "ring-current" intensity of -1.81, while the six-membered rings are calculated to bear



(XXI)

(diamagnetic) "ring-currents" of ca. 0.25. (A more-sophisticated calculation, in which HMO resonance-integrals between bonded atoms are made iteratively self-consistent with corresponding Coulson-bond-orders³⁰, gives qualitatively the same result).

β) t,v bonded, u,w separated by 3 bonds. This will occasion the formation of a six-membered ring (4+2). In this case, P_{tv}^0 is > 0 and large in magnitude; P_{uw}^0 is < 0 and medium. $J^{\text{new ring}}$ is thus positive (i.e., diamagnetic) and 'normal' in size. This is the situation, for example, in the linear acenes (naphthalene, anthracene, etc.), the "ring-current" intensities in which, all positive and within 50% of the benzene value, are well documented in the Literature.^{132,120,155,111,141}

In general, this analysis shows that when the newly formed ring is $4n$ -membered (n an integer), $J^{\text{new ring}}$ is < 0 (i.e., paramagnetic), while when it is $(4n + 2)$ -membered, $J^{\text{new ring}}$ is > 0 (i.e., diamagnetic). This is therefore an extension to certain $4n$ - and $(4n + 2)$ -rings in polycyclic systems, of the now well-known paramagnetic/diamagnetic nature of the $4n$ - / $(4n + 2)$ - monocyclic annulenes.¹⁹⁻²² It should be emphasised, however, that, by this analysis, no comment is claimed on the recently controversial³¹⁰ 'periphery-model'²⁹ of the so-called 'perturbed' annulenes, discussed in detail in Chapter VIII.

In the next sub-section we investigate certain circumstances under which the simple perturbation-theory rules established here may break down. Clearly, if, for example, there is any zero-order degeneracy amongst the energy levels of the two fragments A and B, appropriate linear-combinations of these must be taken.

7.4 Special Cases of A and B Fragments

We distinguish three specific situations:

(i) A, B both Odd-Alternant Fragments

If A and B are both odd-alternant fragments, each will have one electron in a non-bonding MO ($E_0 = \alpha + 0\beta$). A degeneracy must, consequently, arise and appropriate linear-combinations must, therefore, be taken. It has been shown^{20,139} that the removal of this degeneracy leads to non-zero bond-orders between A and B. We must therefore consider how $\bar{\pi}_{(tu)(wv)}$ is affected in these cases.

(a) t, v same parity, u, w same parity. The formulae are essentially as before (§7.3(ii), case (a), equations (7.25) and (7.26)), with a slight modification. In particular

$$\beta\bar{\pi}_{(tu)(wv)} = 2a_{to}b_{uo}b_{wo}a_{vo} / (2x_o) + \text{other terms} \quad (7.30)$$

(the subscript 'o' stands for non-bonding MO's on both A and B).

$\beta\bar{\pi}_{(tu)(wv)}$ will be dominated by the leading term explicitly written in equation (7.30) because x_o will, in general, be small. If t and v are separated by two bonds, and u and w are similarly segregated, a six-membered ring results; then:

$$a_{to}a_{vo} < 0 ; \quad b_{uo}b_{wo} < 0$$

and hence (and, in general, for a $(4n + 2)$ - ring) $J^{\text{new ring}}$ is large and positive. This is the situation which obtains, for example, in the central ring (C) of peropyrene (XVII) and is also the case, in general, with the $(4n + 2)$ - annulenes. (For a $4n$ - ring, $J^{\text{new ring}}$ is, however, still large and negative - see (c), below).

It will now be clear why, in §7.3(ii) (especially in case (a)), we made the stipulation that A and B shall be even-alternant fragments. It is the fact that the central ring of perylene (XII) is constructed by joining two even-alternant fragments (§7.3(ii), case (a)) while that of peropyrene (XVII) is the result of combining two odd-alternant fragments (§7.4(i), case (a)) which is responsible for the very small "ring-current" in ring C of (XII) and the very large one in ring C of (XVII).

(b) t, v different parity; u, w same parity

The non-bonding

(c) t, v different parity; u, w different parity

MO here has no effect and the conclusions are, therefore, the same as for the general case.

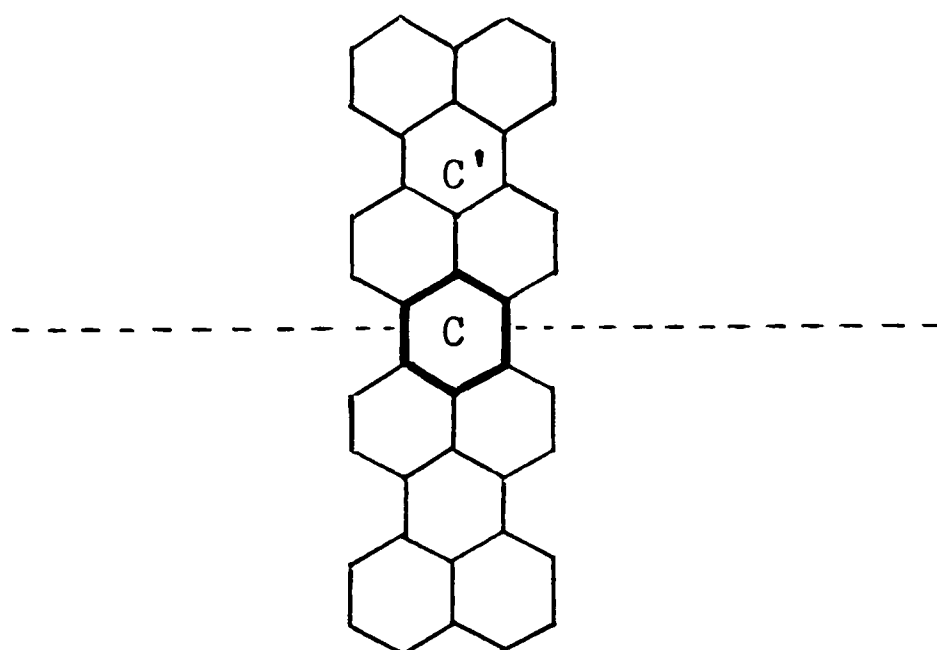
(ii) A and B Identical

If A and B are identical fragments, all zero-order levels are

degenerate in (at least) pairs, and sums and differences of these levels have, therefore, to be taken in the perturbation process. Since all pairs are fully occupied, the effect on the bond orders exactly cancels; the effect on the $\bar{\pi}$ -formulae is thus to change the energies in the denominators. In general, however, the effect is small and the previous qualitative conclusions are valid; (see, for example, the cases of peropyrene (XVII) and perylene (XII), above — §7.4(i), case (a), and §7.3(ii), case (a), respectively).

(iii) A and/or B Large, Coloured, with
Low Ionisation-Energy

As the moieties A and B become larger, the lowest-occupied MO has an x_{μ} -value never exceeding 3, but the highest-occupied molecular-orbitals (HOMO's) can have steadily decreasing x_{μ} , and the approximation of having the x-term in the denominator (as, for example, in equation (7.26)) becomes less valid. The case of quaterrylene (XXII) illustrates this.



(XXII)

The HOMO has

$$x_{\mu} = 0.35$$

while, after degenerate perturbation-theory, the higher of the two pairs of levels has

$$x'_{\mu} = 0.24$$

It is, therefore, not surprising that (although it is still fairly small) $J^{\text{new ring}}$ for ring C of (XXII) (calculated* to be 0.450) is significantly larger than the corresponding quantity (0.239) for ring C of perylene (XII).

7.5 Connection Between Molecular-Orbital Treatment and 'Bond-Fixation' Terminology

It was seen in §7.3(ii) (case (a)) that, in the context of simple MO-theory, when two even-alternant fragments are joined together in such a way as to form a new six-membered ring, like, for example, ring C in perylene (XII), the "ring-current" intensity in that ring is small;

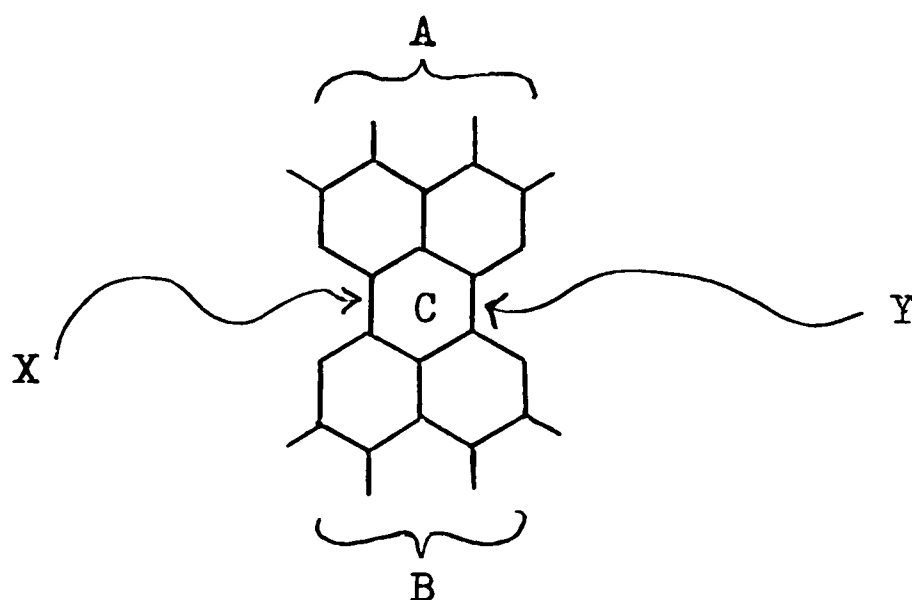


FIGURE 7.2

* See footnote on page 192.

conversely, it was shown in § 7.4(i) (case (a)) that when A and B are both odd-alternant fragments the new ring (such as ring C in peropyrene (XVII)) bears a large "ring-current". In general, even-alternant fragments have at least one Kekulé structure³⁴⁹, while odd-alternant fragments are radicals in the sense that no complete Kekulé-structure may be devised for them. We can therefore say immediately that when fragments A and B are linked together to form a six-membered ring (see Figure 7.2), if fragments A and B both have a Kekulé structure then the "ring current" in ring C will be small, whereas if A and B are both radicals (*i.e.* are therefore devoid of Kekulé structures) the "ring-current" intensity in ring C will be large. We may pursue this reasoning a little further in order to transgress the realms of MO-theory language into that of Valence-Bond Resonance-Theory and in order to say something about 'bond fixation' in the central links X and Y of Figure 7.2. We may distinguish three cases:

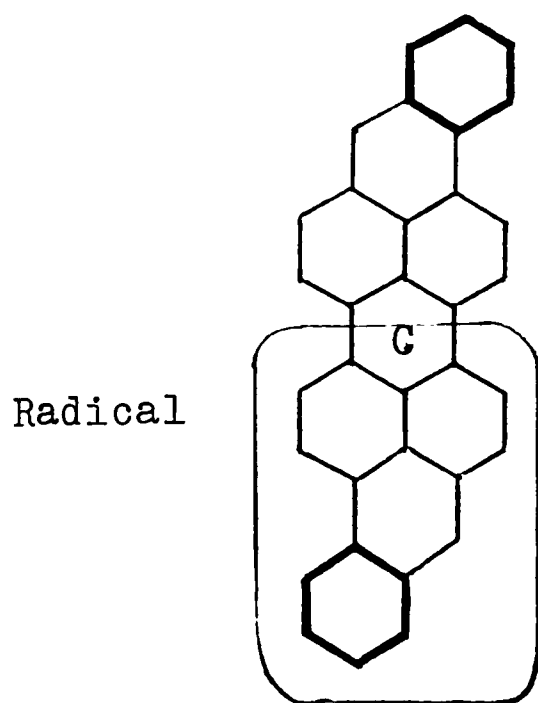
- 1) If A and B are themselves independently possessed of a Kekulé structure, the connecting links X and Y will never appear other than as single links in any Kekulé structure which can be constructed for the composite molecule. (This is the 'perylene' case).
- 2) If A and B are both radicals, at least one Kekulé structure can always be devised for the composite molecule; furthermore, in this Kekulé structure, either X or Y will, of necessity, be represented as a double bond. (This is the 'peropyrene' case).
- [3) If, of A and B, one is possessed of a Kekulé structure and the other is a radical, then the composite molecule is also a radical and hence need not further concern us here.]

7.6 Numerical Examples and Comparisons with Experiment

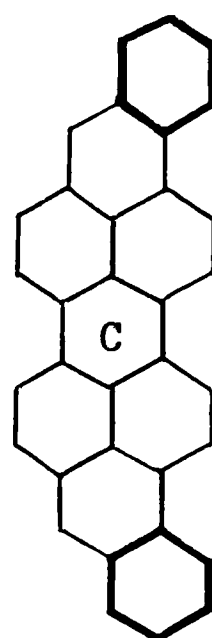
(i) Examples Related to Perylene and Peropyrene

The points made in §7.5 are illustrated by the following examples:

(1) 1,2;8,9 - and 1,2;9,10 Dibenzoperopyrene (XXIII) and (XXIV))



(XXIII)

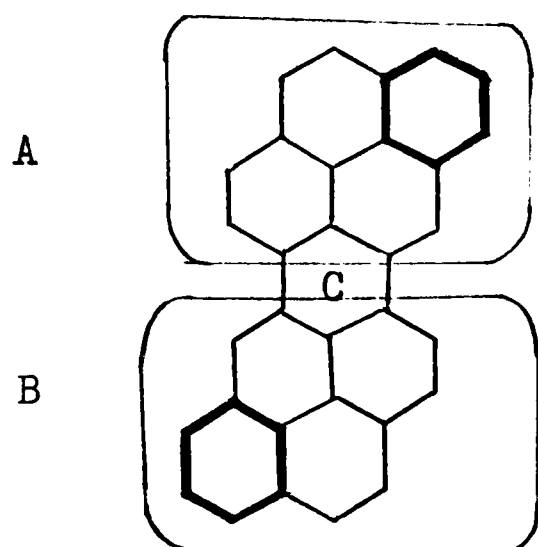


(XXIV)

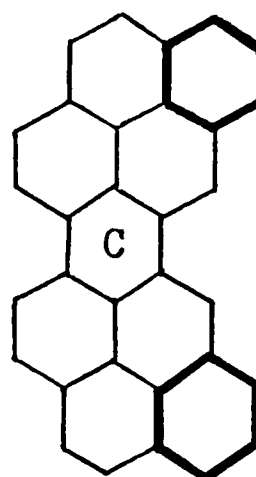
If two further rings are added to peropyrene (XVII) in such a way as to preserve the radical nature of the fragments A and B, giving, for example, (XXIII) or (XXIV), the "ring-current" intensities in the central ring, C, remain large — a full calculation (see footnote on p 192) predicts the intensity of the current in rings C of (XXIII) and (XXIV) to be 1.377 and 1.345, respectively).

(2) 1,14;7,8 - and 1,14;10,11 Dibenzoperopyrene (XXV) and (XXVI)).

If two further rings are added to peropyrene (XVII) in such a way as to destroy the radical nature of the fragments A and B, so that Kekulé structures can be written for them, the situation in §7.4(i) (case (a)) is transformed to that described in §7.3(ii) (case (a)) — i.e., a 'peropyrene' arrangement has been converted to a 'perylene' one and, as a result, the "ring-current" intensity in the central ring, C, falls dramatically. Thus, if two rings are added to peropyrene to form (XXV) or (XXVI), the fragments A and B which result both possess



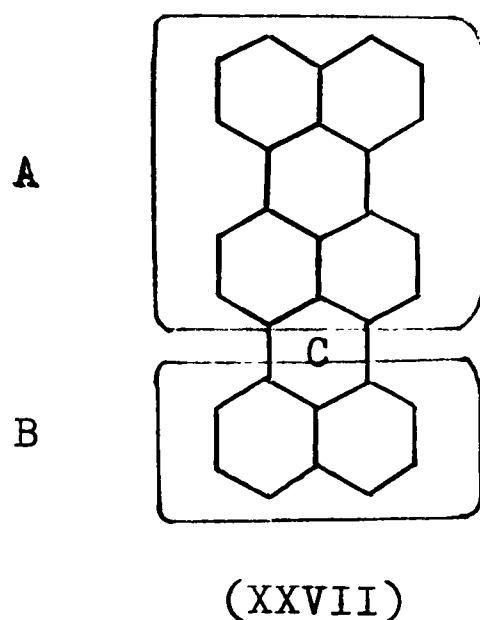
(XXV)



(XXVI)

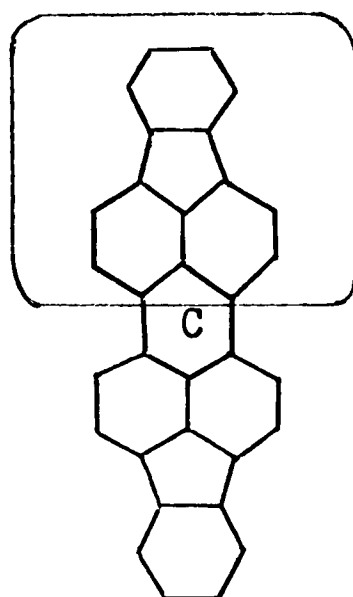
full Kekulé-structures (in fact, in the present example, A and B both have the carbon-atom connectivity of pyrene) and the "ring-current" intensity in ring C (calculated to be 0.311 for both (XXV) and (XXVI)) is, accordingly, very similar to that in the corresponding ring in perylene (XII). In fact, despite their names, (XXV) and (XXVI) might, in this respect, more properly be regarded as being formally derived from perylene, rather than peropyrene.

(3) Other Examples : The molecule terrylene (XXVII) might usefully be considered as one of the 'perylene' type of molecules, in which fragment B has the carbon-atom connectivity of naphthalene while fragment A has the connectivity of the perylene molecule itself. Accordingly, the "ring-current" intensity in ring C is calculated to be 0.321 — not as low as in the corresponding ring in perylene, because the B-fragment is larger (§7.4(iii)). In the same way, ring



C in quaterrylene (XXII) may be considered to be of the 'perylene' type, since it is formed from fragments A and B, each of which has a Kekulé structure — in fact, in this case, both the fragments A and B have the carbon-atom connectivity of the perylene molecule itself! As discussed in §7.4(iii), however, both fragments are large and so the "ring-current" intensity in ring C of (XXII), though still quite small (0.447), is significantly larger than that (0.239) in the corresponding 'central' ring, C, in perylene (XII). This kind of argument can be taken further: ring C' of (XXII) might be thought of as being formed, via the sort of perturbation process we are considering, from a 'naphthalenic' fragment and from a fragment which had the carbon-atom connectivity of the terrylene molecule (XVII) — each of which is itself possessed of a Kekulé structure. The low calculated-"ring-current" intensity is entirely in accord with this view.

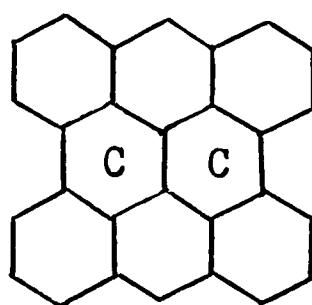
(4) Other Cases : Finally, we note two situations which are not covered by the analysis so-far outlined but to which the above qualitative solutions seem, numerically, to apply. In §7.3(ii) we restricted the discussion to those cases in which the fragments A and B were even alternants; the restriction concerning the even nature of these alternant fragments was relaxed in §7.4(i) but, although the final composite-molecule might be non-alternant (as, for example, is fluoranthene (XX)), we have not formally considered the ramifications of the individual fragments themselves'being non-alternant. Such would be the case, for example, if two fragments each with the carbon-atom connectivity of fluoranthene itself were brought together to form periflanthene (XXVIII). The "ring-current" intensity in the central



(XXVIII)

ring, C, is, from a full McWeeny-calculation, only 0.037. Another situation not strictly covered by our present analysis is the formation of two new rings when two even-alternant fragments are brought together

in a perturbation process analagous to (but not the same as) the one schematically depicted in Figure 7.1 — for example, the formation of anthanthrene (XXIX) from two fragments which have the carbon-atom



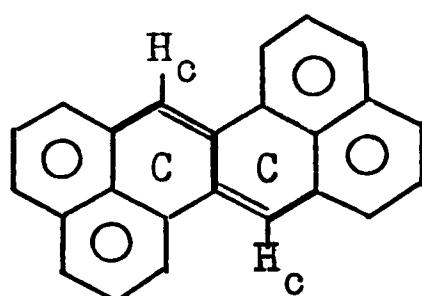
(XXIX)

connectivity of anthracene. The "ring-current" intensity in rings C is 0.442 — higher than that in perylene (XII), ring C (0.239), but almost exactly the same as, for example, that (0.447) in the central ring (C) of quaterrylene (XXII).

(ii) Examples in the Zethrene Series

We have so far established a relation between the "ring-current" intensity in the central rings of molecules related to peropyrene (XVII) and perylene (XII) and the presence or absence of 'single-bond fixation' from the resonance-theory Kekulé-structure point of view. The obvious way to attempt to verify these predictions experimentally is by ^1H -NMR measurements. However, in molecules related to (XII) and (XVII) the 'small' or 'large' "ring-current" is in a ring (the central one) which has no protons attached to it; hence, the "ring-current" intensity in this ring has only a second-order effect on the chemical

shifts of the protons (all attached to other rings) in these molecules. We therefore attempt to extend these ideas to another series of hydrocarbons in which, on simple VB-Resonance-Theory concepts, there are fixed single and double bonds in rings to which protons are directly bonded: predictions on this type of molecule are, therefore, more susceptible to experimental test. Such a series is zethrene (XXX) — see also §6.4(iv) — and its homologues. In (XXX) the bonds in rings C

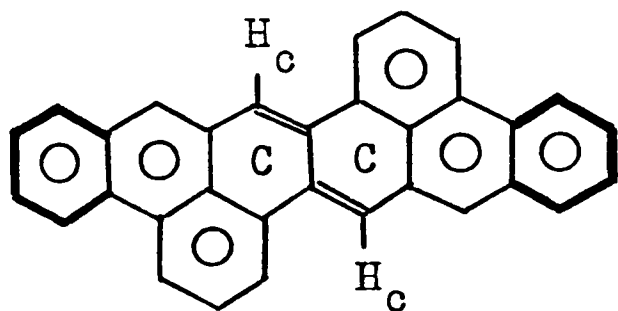


(XXX)

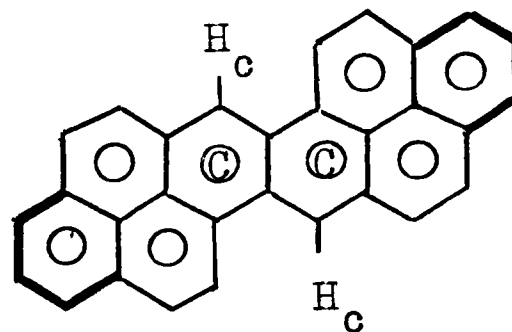
indicated by double lines are always double, and those depicted with thick, single lines are always single, in any Kekulé structure which can be devised for the molecule as a whole.³⁴² The calculated "ring-current" in rings C is only 0.365 (see §6.4(iv) and ref. 141); accordingly, the ratio $(B'_r / B'_{\text{benzene}})^*$ for the protons (H_C) attached to rings C in zethrene is calculated to be only 0.853; from equation (1.98) this implies a chemical shift for this proton of about 3.0τ — i.e. upfield of benzene (2.73τ ¹⁷⁴). Now formally condensing two further rings onto zethrene in such a way as to preserve the 'bond-fixation' — e.g. forming 4,5; 11,12 dibenzozethrene (XXXI) — leaves the "ring-current" intensity in the central rings (C) essentially unchanged (0.363), and the 'sigma ratio' $(B'_r / B'_{\text{benzene}})$ of the protons indicated,

* See page 60

attached to these central rings, is now 0.915, implying (from equation (1.98)) a chemical shift of ca. 2.9τ . The protons H_c in (XXX) and (XXXI) thus both have sigma ratios lower than the benzene proton (sigma ratio of unity) which is at the lower end of the range (1.0 - 2.1) of sigma ratios previously encountered.^{170,171,140,141} If, however, we formally add two further rings to zethrene in such a way as to remove the bond-fixation — forming, for example, 3,4; 9,10 dibenzozethrene (XXXII) — the calculated "ring-current" intensity in the central ring



(XXXI)



(XXXII)

goes up dramatically to 1.355 and the sigma ratio of the proton attached to this central ring is as high as 2.170, which results (after application of equation (1.98)) in a predicted ^1H -NMR chemical-shift of 0.95τ . This is also outside the range (1.0 - 2.1) of previously encountered sigma-ratios — but in the opposite direction from that of H_c in (XXXI). We thus arrive at the rather entertaining observation that, by taking (XXXI) and simply changing slightly the position of substitution of two of the rings to give (XXXII), the chemical shift of the protons marked " H_c " in (XXXI) and (XXXII) is caused to leap-frog the entire range of previously observed sigma-ratio values!

The chemical-shift differences between the protons H_c in (XXXI) and (XXXII) is thus predicted to be ca. 2.0 ppm. Since, under the appropriate experimental-conditions,^{60,174,38a} chemical shifts in these

molecules may be measured to within 0.005 ppm, this prediction in principle affords the opportunity of a singularly reliable experimental test. Proton chemical-shifts for zethrene (XXX) are available, as are those for 4,5; 11,12 dibenzozethrene (XXXI) (by the kind help of Professor E. Clar³⁴⁷); however, 3,4; 9,10 dibenzozethrene (XXXII) has, unfortunately, not been synthesised, and, according to Clar³⁵¹, it is likely to be a difficult molecule to make. It is to be hoped that the central importance of this molecule in testing the theoretical implications of "ring-current" theory discussed in the present chapter may provide some incentive for its eventual synthesis.*

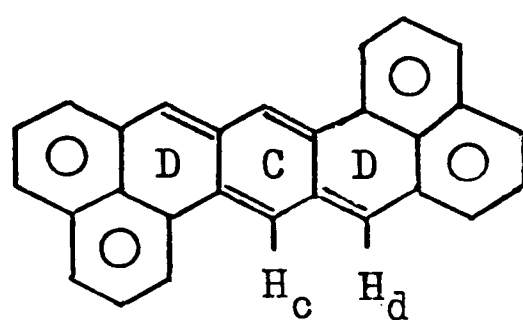
We have so far neglected to mention that the protons H_c in (XXXI) and (XXXII) (as well as in (XXX)), all being what, on Martin's nomenclature²⁴¹, are called 'H α 3' protons, will be involved in van der Waals steric-interactions which are thought (§§1.7 and 2.5(ii)) to displace the ^1H -NMR shifts of such protons ca. 0.6 ppm downfield (i.e. to lower τ -values)[†]. Since these steric interactions, if they are genuine, will be approximately the same for the protons H_c in both (XXXI) and (XXXII), our prediction still stands that the chemical shifts of these two sets of protons should differ by ca. 2.0 ppm.

An exactly analogous trend is observed in a series of molecules (XXXIV) and (XXXV) similarly derived from heptazethrene (XXXIII).

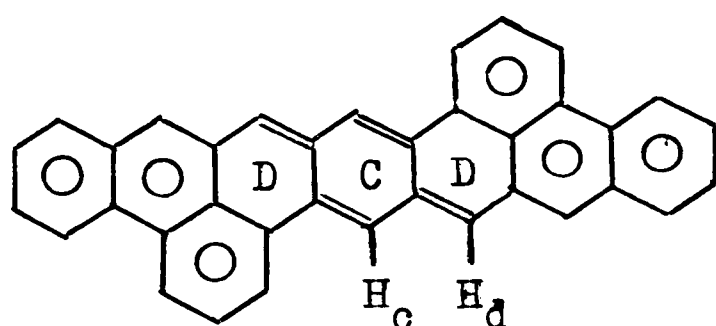
This series has the desirable feature that each molecule in it contains protons, H_d , attached to rings (D) bearing (in the case of (XXXIII) and (XXXIV)) low, or (in the case of (XXXV)) high, "ring-currents", which are

* Historical Note: It is of interest to record here that the relative chemical-shifts of H_c in (XXXI) and (XXXII) have been rationalised by Clar by means of his "Aromatic-Sextet" arguments.^{342,352} In a letter to the author of December 31st, 1970, he wrote³⁴⁷: "I was interested to learn that your calculation leads to the same results as the strict application of the aromatic sextet".

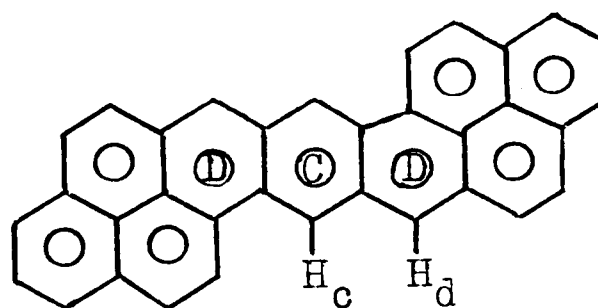
[†] But see Appendix B.



(XXXIII)



(XXXIV)



(XXXV)

not subject to any hydrogen-hydrogen steric-interaction. Data for this series are summarised in Table 7.2.

TABLE 7.2

Data for Molecules Formally Derived from Heptazethrene (XXXIII)

Molecule	"Ring Current" in Rings [†]		Sigma Ratios ^{††} of Protons		Chemical Shifts ^{**} of Protons	
	C	D	H _c	H _d	H _c	H _d
Heptazethrene (XXXIII)	0.577	0.410	0.985	0.810	* 2.80τ	3.08τ
4,5: 12,13 Dibenzohepta- zethrene (XXXIV)	0.574	0.405	1.021	0.849	* 2.75τ	3.02τ
3,4; 11,12 Dibenzohepta- zethrene (XXXV)	1.447	1.252	2.284	1.941	* 0.78τ	1.31τ

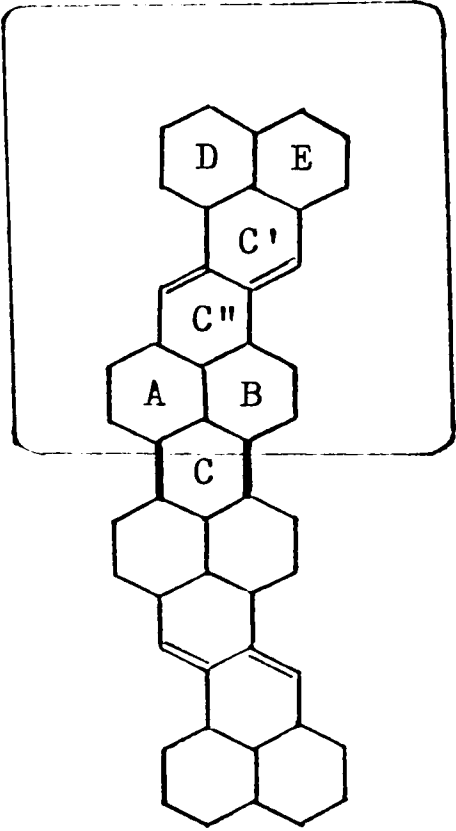
* Exclusive of a steric contribution of ca. 0.6 ppm downfield (i.e. the observed shift of H_c in heptazethrene would be expected to be ca. (2.80 - 0.60)τ = ca. 2.2τ)

† By the full method described in the footnote on page 192.

†† From the calculated "ring-currents" in the previous two columns, equation (1.96) and the procedure described on page 60.

** From the sigma ratios in the previous two columns, and equation (1.98).

From Table 7.2 it is seen that the chemical shifts of H_c in (XXXIV) and (XXXV) should differ by ca. 2.0 ppm, while those of H_d in the two molecules should differ by ca. 1.7 ppm. The H_c-protons suffer steric interactions and so the actual shift of H_c in (XXXV) would be in the region of 0.2τ — nearly as low a τ-value as that of proton 9 in 1,2;7,8



(XXXVI)

TABLE 7.2
"Ring-Current" Intensities in
(XXXVI)

"Ring-Current" Intensity in Rings						
C	C'	C''	A	B	D	E
0.706	0.462	0.640	0.846	0.968	0.895	0.824

dibenzanthracene (XV) which partially achieves this low τ -value by experiencing a double steric-interaction (see §2.5(ii)). The H_c -protons of (XXXIII) and (XXXIV) appear from Table 7.2 to resonate to high field of benzene; in practice, because of the steric interactions just mentioned, they will be to low field of the benzene signal ($2.73\tau^{1.74}$). The H_d -protons of (XXXIII) and (XXXIV) are, however, sterically unhindered and hence would be expected to come into resonance at the τ -values indicated in the Table; these protons would thus resonate ca. 0.3 ppm to high field of benzene — a quite remarkable occurrence for a proton in the molecular plane of a planar, conjugated hydrocarbon composed entirely of condensed, hexagonal rings and, furthermore, containing as many as nine of them! (cf. refs 38 and 141).

(ii) A 13-Ring Hydrocarbon Related to
Zethrene and Perylene

We conclude this section on numerical examples by considering a very large (and, as yet, hypothetical) molecule which is related both to zethrene and to perylene; we form it by notionally combining together two zethrene-like fragments X and Y in the kind of perturbation scheme envisaged in §7.3(ii), creating, in the process, a new ring, C (XXXVI). Since the two zethrene-like fragments, X and Y, possess a Kekulé structure, the ring C in (XXXVI) is formally analogous to ring C in perylene (XII), and its central linkages (the 'new' bonds formed during the perturbation process) are, therefore, 'fixed', single bonds in the sense in which this term has been used previously (§7.5). Furthermore, the bonds which are 'fixed' as double in the two zethrene-fragments (those indicated as double in rings C' and C'' of (XXXVI) and their symmetry equivalents in fragment Y) are also 'fixed' in the composite molecule. On this basis, we should therefore perhaps naïvely expect very low

"ring-current" intensities in rings C, C' and C'' of (XXXVI); because, however, the fragments X and Y are 'large and coloured' (§7.4(iii)), the "ring-current" intensities in rings C, C' and C'' of (XXXVI), though small (see Table 7.3), are not as low as in the analogous rings with correspondingly 'fixed' single- and double bonds in perylene (XII) and zethrene (XXX). In fact, the "ring-current" intensities in these rings are not much smaller than those computed for the other distinct rings, A, B, D and E, of (XXXVI). (See Table 7.3). All "ring-current" intensities in the molecule are actually smaller than that in benzene, with the result that although (XXXVI) has 13 rings, the 'London' (i.e. "ring-current") contribution to the magnetic susceptibility perpendicular to its molecular plane is predicted to be only about ten times (in fact, 9.976 times) the benzene value.

7.6 Conclusions

In this chapter we have succeeded in providing a theoretical basis for relating 'high' and 'low' "ring-current" intensities to intuitive Valence-Bond-Resonance-Theory (VB-RT) ideas about 'bond fixation'.

It should be noted that this aim has not been achieved by devising a "ring-current" formalism which is itself actually based on a VB-RT

wave-function; (this is, however, an approach which is currently being followed^{236,353}). The philosophy which we have adopted here has been

1) To identify and classify those situations in which simple MO-theory predicts specific rings in conjugated hydrocarbon-systems to have exceptionally high or low "ring-currents", and then

2) To use topological arguments which rely simply on the carbon-atom connectivities of the conjugated systems in question to show that the situations identified in 1), above, are just those in which the absence or presence of VB-RT 'bond-fixation' is to be expected.

In invoking these topological considerations, we have implicitly been making use of, though have not often lately referred to, the techniques of graph theory. In Chapter VI, it was concluded that the "ring-current" index is not a completely topological quantity, even when a purely topological wave-function (such as the simple Hückel one adopted in the present calculations) has been used to calculate it. This is because the expression for the "ring-current" intensity based on such a wave function (equation (6.15)) explicitly involves the areas of the various rings of the conjugated system, as well as the bond orders and imaginary bond-bond polarisabilities derived from the topological wave-function (see Appendix D). Furthermore, before these bond orders and polarisabilities may be calculated from the eigenvectors and eigenvalues of the topological wave-function (Appendix D), some external prescription — 'external', that is, to the topological considerations — such as the Aufbau Principle is additionally required in order to distribute the π -electrons of the system amongst the available topological-orbitals (eigenvalues). (This aspect has recently been investigated in some detail by the present author and Rouvray — see ref. 303). The point we wish to make, in conclusion, however, is that in dealing with entirely condensed, benzenoid hydrocarbons (to which class 19 of the 22 molecules specifically referred to in this chapter belong) we assume that all ring areas are approximately the same as the area of a standard benzene-hexagon. In this very special case, therefore, once given the Aufbau Principle,³⁰³ "ring-current" intensities calculated from a simple HMO ('topological') wave-function are dependent only on the carbon-atom connectivity (i.e., the 'topology') of the benzenoid hydrocarbon in question because all rings in such a molecule are taken to have unit area. A comparison between the predicted ¹H-NMR chemical-shifts of the protons attached to ring C in (XXXIV) and (XXXV) reveals just how dramatic such changes

in carbon-atom connectivity can be (§7.6(ii)). Finally, if the occasional five-membered ring (area ca. 0.66 that of a standard benzene-hexagon) and/or seven-membered ring (area ca. 1.40 benzene-hexagon units) were present in a molecule consisting predominantly of hexagonal, benzenoid rings, the error introduced into calculated "ring-current" intensities by neglecting these differences in ring area would never be greater than 40% and, because of the way in which the ring-area factor plays its part in determining "ring-current" sizes, would usually be considerably less than this. That is why, in proposing the qualitative and semi-quantitative arguments about 'high' and 'low' "ring-currents" in §§7.3 and 7.4, it was not considered necessary to make specific reference to individual ring-areas.

PART FOUR

NON-ALTERNANT HYDROCARBONS
AND STRONGLY PARAMAGNETIC
CONJUGATED-SYSTEMS.

CHAPTER VIII

STRONGLY PARAMAGNETIC CONJUGATED-SYSTEMS

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CHAPTER VIII

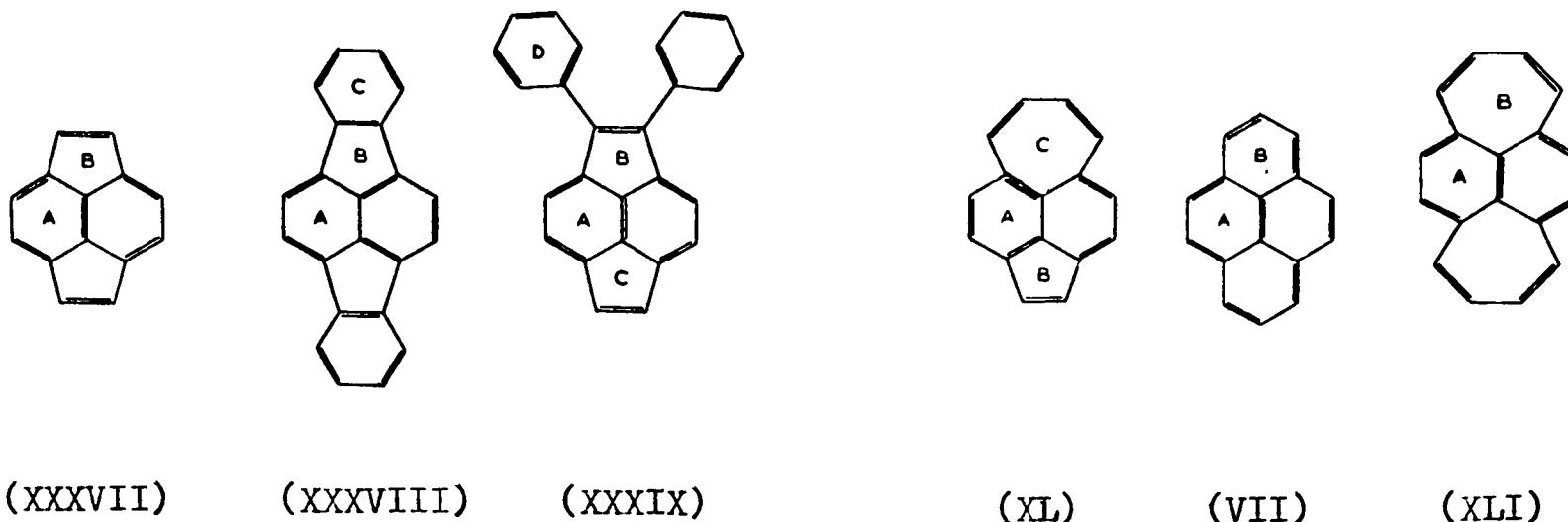
STRONGLY PARAMAGNETIC CONJUGATED-SYSTEMS*

8.1 Summary of the Chapter

In this, the penultimate Part of this Thesis, we shall extend the range of molecules studied by using simple, and more-sophisticated, theories of the "ring-current" effect to investigate the 'London' π -electron magnetic-properties of a family of conjugated systems which appear to bear large paramagnetic "ring-currents", and will thereby discover the quantitative limits to which these simple theories of the "ring-current" effect (which have been the prime concern of this Thesis) may be pushed. In Part II of the Thesis, attention was confined solely to condensed, benzenoid hydrocarbons, all of which are unambiguously diamagnetic; in Part III, certain diamagnetic non-alternant molecules (such as fluoranthene (XX)), as well as some paramagnetic alternant ones (such as biphenylene (XXI)), were encountered. In the present chapter, we shall focus attention on pyracylene (XXXVII) and some related molecules (XXXVIII) and (XXXIX)), the ^1H -NMR spectra of which have been interpreted by Trost et al.²⁹ in terms of paramagnetic "ring-currents". These workers claimed that such an interpretation provides support for the postulate that pyracylene can be regarded as a [12]-annulene with

* Some of the material reported in this chapter has been published. The full reference is:
C.A. COULSON and R.B. MALLION, "On the Question of Paramagnetic "Ring-Currents" in Pyracylene and Related Molecules", J.Amer.Chem.Soc., 1976, Vol. 98, pp. 592-598.

Historical Note: Copies of correspondence with the late Professor Coulson concerning some of the subject matter of this paper (as well as correspondence with reviewers and referees) have been deposited (under file B. 41. 27) with the Coulson Papers in the Contemporary Scientific Archives Collection of the Bodleian Library, University of Oxford.



an internal vinyl cross-link and that it should, therefore, be a good model for a planar $[12]$ - annulene. In order to test this experimental deduction we shall carry out a series of semi-empirical MO-calculations (of varying degrees of sophistication) on molecules (XXXVII) - (XXXIX); in addition, we shall examine the "ring currents" in acepleiadylene (XL), a non-alternant isomer of pyrene (VII) which could formally be considered as a "perturbed" $[4n+2]$ - annulene, and in dipleiadiene (XLI) which, like pyracylene, has a $4n$ - periphery (with, in this case, $n=4$). In the discussion we shall draw attention to the apparent importance of using a realistic geometry, rather than an idealised one, when calculating the magnetic properties of conjugated molecules whose π -electron systems are predominantly paramagnetic.

8.2 Background

Trost et al.²⁹ have pointed out that one of the major frustrations of trying experimentally to verify theoretical predictions about the properties of $4n$ -monocyclic systems is the molecular flexibility and general non-planarity of such systems larger than cyclobutadiene. In an attempt to rectify this, Trost and his co-workers²⁹ resolved to introduce molecular rigidity into a basic $4n$, annulenic, monocyclic

system by incorporating cross-links; in particular, they investigated the perturbation arising as a result of the insertion of an internal π -system into a monocyclic periphery, producing, for example, pyracylene (XXXVII) (a 'perturbed' $4n$ -peripheral system in which $n=3$) (see structure (1a) of Figure 8.1); they also discussed the previously

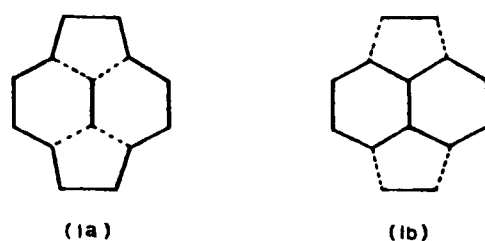


FIGURE 8.1

synthesised 1,2; 5,6 dibenzopyracylene (XXXVIII) which may formally be considered as being derived from a $4n$ -periphery (where, in this case, $n=5$) by the addition of an "internal" π -system and two other cross-links.

There is, however, another way to visualise pyracylene — as a "naphthalene" core, plus two "vinyl" bridges (structure 1b of Figure 8.1). Lo and Whitehead,³¹ after calculating the ground-state electronic-properties of pyracylene via an SCF ($\pi + \sigma$) method, considered that, on balance, neutral pyracylene is more aptly described by structure 8.1b than by the peripheral model depicted in structure 8.1a. Yamaguchi and Nakajima^{32,33} have also concluded that the up-field shift of the ^1H -NMR spectrum, and the unusually low value of the first half-wave potential of pyracylene, can be well explained in terms of (respectively) the diamagnetic anisotropy and the energy of the lowest-vacant SCF-MO, calculated on the basis of the predicted equilibrium-configuration which corresponds to the "naphthalene-core" model represented by structure 1b of Figure 8.1. Since then, Yamaguchi and Nakajima³² have conjectured that the periphery of pyracylene may bear a paramagnetic "ring-current" characteristic of the $4n$ -perimeter but that, on the other hand, the

naphthalene core in pyracylene "may exhibit a diamagnetic 'ring-current' to the same extent as a free naphthalene molecule"³²

In the present chapter, we attempt to throw some light on these speculations, and also to test how far simple theories of the "ring-current" effect can be stretched, by performing "ring-current" calculations on (XXXVII) - (XXXIX), in acepleiadylene (XL) (a non-alternant analogue of pyrene (VII)), and dipleiadiene (XLI); these calculations will be based on variants of the simple London theory, and on ostensibly more-sophisticated SCF-versions of it.

8.3 Calculations

Six types of calculations were performed, according to the following methods:

- (1) Simple Hückel-London-McWeeny approach¹³², via equations (3.33) and (6.15) and the assumptions detailed in the footnote on page 192
- (2) As above but based on an iterative Hückel wave-function which is self-consistent with respect to resonance integrals and calculated bond-lengths and with respect to Coulomb integrals and calculated atomic-charges. In this approach, the resonance-integral — bond-order relationship used was that of Coulson and Golebiewski³⁵⁴ and, in considering variations of Coulomb integrals with charge distribution within the molecule, not only the charges on the nearest-neighbour atoms but, in addition, those of second-nearest neighbours were also taken into account (as per the method of Kuhn,³⁵⁵ discussed in detail by Coulson and Wille³⁵⁶ and previously applied to the calculation of the magnetic susceptibilities of conjugated systems by Gayoso and Boucek^{165,357}). This whole procedure, iteratively self-consistent with respect to charges and bond orders, has been called^{357,165} the 'iterative β ω ' ω ' ' method and it arguably represents the best available

calculation of its type. Such a calculation on pyracylene (XXXVII) and dipleiadiene (XLI) (based on regular geometries and on the parameters of Kuhn³⁵⁵ and of Coulson and Golebiewski³⁵⁴) required 25 iterations.

- (3) Hall-Hardisson Coupled-Hartree-Fock approach¹⁹² (described in §1.4(ii)(b)). In these calculations, based on a Pariser-Parr-Pople^{201,202} π -electron wave-function, with fixed resonance-integrals, the parametrisation used was that of Lazzeretti and Taddei^{176*}; (i.e., the α core-integrals were calculated via the Goeppert-Mayer and Sklar³⁵⁸ formalism, the γ integrals were estimated by the procedure of Nishimoto and Mataga,³⁵⁹ 11.08eV (ca. 1068 kJ mol⁻¹) was taken as the mono-centric repulsion-integral for carbon, 11.42 eV (ca. 1101 kJ mol⁻¹) as the ionisation potential of carbon, and the β -parameter was set at -2.39eV (ca. -230 kJ mol⁻¹). Twelve iterations were required for the SCF-convergence (convergence criterion: 1 in 10⁷), and 60 cycles were necessary for the convergence of P' , the first-order correction to the bond-order matrix (brought about by the presence of the external magnetic-field and calculated by the Coupled-Hartree-Fock procedure of Hall and Hardisson¹⁹² — see §1.4(ii)(b) for details).
- (4) Coupled-Hartree-Fock, Hall-Hardisson¹⁹² method based on a PPP-SCF wave-function^{201,202} (as in (3), above), but with variable resonance-integrals, iterated so as to be self-consistent with respect to the corresponding calculated bond-orders. This is an approach which Ege and Vogler¹⁷⁹ have found useful for paramagnetic systems.
- (5) Coulson-Gomes-Mallion¹⁶² method based on a PPP-SCF wave-function^{201,202}

* I am very grateful to Professor F. Taddei and Dr. P. Lazzeretti of the University of Modena, Italy, for kindly making available their program, offered in ref. 176.

with fixed resonance-integrals.* All the approaches considered in (1) - (4) invoke the London integral-approximation (see §1.4(i)(e) and §1.4(iii)). In a recent paper, however, (discussed in §1.4(iii)) Coulson, Gomes and the present author¹⁶² derived an exact expression for $\chi_{\perp}^{\pi}$, the total π -electron contribution to the magnetic susceptibility perpendicular to the molecular plane of a polycyclic, conjugated hydrocarbon. Once given P' , this expression makes no further appeal to the London integral-approximation. The consequence of this procedure is that the total $\chi_{\perp}^{\pi}$ is split into two parts — one, $\chi_{\perp}^{\pi \text{ London}}$ (due to what we term the "integrated π -electron current-densities" around the rings), corresponds to that part of the total $\chi_{\perp}^{\pi}$ which would have been calculated anyway, even if the London approximation had been made, and the other, $\chi_{\perp}^{\pi \text{ non-London}}$ (comprising what we have called the 'bond' and 'non-bond' moments), corresponds to what might be considered as the 'local' π -electron contribution to $\chi_{\perp}$. In most calculations which lose this latter term by invoking the London approximation, its effect is conveniently incorporated into the empirically determined, 'local' σ -contributions, when comparisons with experiment are to be made.

Another feature of this approach is that it does make provision for breaking down the total $\chi_{\perp}^{\pi}$ into contributions associated with each individual ring of a polycyclic, conjugated system. This idea is particularly significant when just $\chi_{\perp}^{\pi \text{ London}}$ is considered, for it is

* I am most grateful to Dr. J.A.N.F. Gomes, (Linacre College), now of the University of Porto, Portugal, for help with calculations based on the method of Coulson, Gomes and the present author;¹⁶² these were carried out by use of a program which Dr. Gomes prepared for the Oxford-University ICL 1906A computer. This program had been used to produce the results reported in ref. 162.

then possible to calculate "integrated π -electron current-densities" which will be a characteristic of each ring of a polycyclic molecule and which are analogous to what the London-McWeeny¹³² method would identify with the "ring-current" intensities in the corresponding rings. The calculation of such quantities is not straightforward in the Hall-Hardisson method¹⁹² as originally presented.

(6) As above, but with variable resonance-integrals, iterated so as to be self-consistent with respect to the corresponding bond-orders. Desirable features of this approach are (a) minimal use of the London integral-approximation, (b) iteration of resonance integrals with respect to calculated bond-length, as will be seen (§8.4(iv)) to be particularly appropriate for strongly paramagnetic conjugated-systems.

8.4 Results and Discussion

(i) Simple HMO-Calculations

It can be seen from Table 8.1* that, on the basis of the approximations inherent in this "topological" calculation (which required knowledge only of the carbon-atom connectivity and of the areas of the various constituent-rings of each polycyclic system), pyracylene is indeed predicted to sustain paramagnetic "ring-currents", even in its six-membered rings; the five-membered rings bear a much larger paramagnetic current, however, and so, in spite of their smaller area (ca. 0.66 times that of a standard benzene-hexagon), they will still make the major contribution to the overall "London" magnetic-susceptibility

* In this Part of the Thesis, Tables are once again, for convenience, collected together at the end of the chapter.

of pyracylene, perpendicular to its molecular plane; 1,2:5;6-dibenzopyracylene (XXXVIII), on the other hand, even though it does have a $4n$ periphery, bears a paramagnetic "ring-current" only in its five-membered rings. 1,2-Diphenylpyracylene (XXXIX) merely displays the expected "ring-current" behaviour of phenyl-substituted polycyclic-hydrocarbons, i.e., that the "ring-current" intensities in the moieties joined by the 'single' bond are just slightly modified renditions of those extant in the original, unsubstituted molecules. Thus, because (as far as the "ring currents" are concerned) phenyl substitution represents a fairly small change in the pyracylene system (or, more precisely, because the imaginary bond-bond polarisabilities—see §1.4(i)(i) and Appendix D—between a given bond in one of the phenyl groups and any other bond in the conjugated system outside the given phenyl ring are zero), the phenyl (diamagnetic) "ring-currents" in (XXXIX) are changed by only about 12% from the benzene value of +1, to ca. 0.88 (cf. biphenyl, with a "ring-current" intensity^{*}, from a purely "topological" calculation, of 0.93₅), and those of the pyracylene moiety all remain paramagnetic (see Table 8.1). The pattern of "ring-current" intensities in (XXXIX) is at least qualitatively consistent with the ¹H-NMR spectra of this molecule (and related ones) reported by Trost et al.²⁹

We note that, on the basis of the idealised geometries adopted here and the "ring currents" presented in Table 8.1, the London contribution to magnetic susceptibility in (XXXVII) – (XXXIX) (on the

* London's value³ for the "ring-current" intensity of biphenyl is incorrect; McWeeny's result^{135,146} is, however, accurate, as a further calculation by the present author has confirmed.

undoubtedly unjustified assumption that the latter is planar), expressed as a ratio to that of benzene, and calculated, for example, via equations (3.17) - (3.20), are: -3.83, + 1.43, and -1.54, respectively. On the basis of this topological calculation, the 'mobile' π -systems of (XXXVII) and (XXXIX) would thus appear to display overall paramagnetism, while that of (XXXVIII) would be expected to exhibit a net diamagnetism.

It is instructive, at this stage, to consider the "ring-current" intensities in acepleiadylene (XL), calculated by this topological approach. One might perhaps formally regard acepleiadylene as the $[4n+2]$ -periphery analogue of pyracylene obtained by replacing one of the five-membered rings of this latter molecule by a seven-membered cycle. Acepleiadylene (XL) is, furthermore, a non-alternant isomer of pyrene which itself might, therefore, also be considered formally as, in some way, a perturbed $[4n+2]$ -annulene. The repercussions of this change on the "ring-current" intensities are quite dramatic (as Table 8.2 clearly shows), those in acepleiadylene being large and unambiguously diamagnetic — quite the same order, in fact, as those encountered in the alternant, condensed, benzenoid hydrocarbons and, in particular, similar in magnitude to the currents^{120,140} in pyrene (VII), its alternant isomer which also has a $[4n+2]$ -perimeter (see Table 8.2). On the basis of this 'topological' calculation, therefore, it seems that acepleiadylene, too, might equally be considered (as far as its "ring currents" are concerned) as a 'perturbed' annulene. This proposition at least seems to be consistent with the experimental ¹H-NMR data⁹ available for this molecule.

Finally, formal replacement also of the second five-membered ring in pyracylene leads to the (hypothetical) molecule dipleiadiene (XLI) which, once more, like pyracylene, has a $4n$ periphery (this time with

$n=4$); again, as expected, this 'topological' calculation unambiguously predicts paramagnetic "ring-currents" in all rings, as indicated in the last row of Table 8.2.

(ii) $\beta\omega'\omega''$ Iterative
Calculation on Pyracylene

The results of the 'topological' calculation on pyracylene were by no means confirmed by the $\beta\omega'\omega''$ calculation (which was iteratively self-consistent with respect to charges and bond orders), as Table 8.3 indicates. By the time convergence had been achieved, Coulomb integrals had been corrected by up to ca. $\pm 0.055\beta$, while resonance integrals varied from ca. 1.11β for the 'fixed' double-bond in the five-membered ring, to ca. 0.85β for the 'single' bond in that ring. This calculation still gave the qualitative result that there is a paramagnetic "ring-current" in the five-membered ring of pyracylene, though of much reduced intensity (-1.01 as compared with the value of -2.32 arising from the topological calculation); however, the iterative calculation predicts that there should be a small but nevertheless diamagnetic "ring-current" in the six-membered (benzenoid) ring. In a commonly used terminology (e.g., ref 360), the five-membered ring of (XXXVII) would be described as being paratropic and the six-membered ring of pyracylene, on the basis of this iterative calculation, is diatropic. The overall 'mobile' π -electron magnetic-susceptibility is still predicted to be paramagnetic but because two rings which, from the topological calculation, were thought to be paratropic are now predicted to be diatropic, while the "ring-current" intensity in the two rings which are still expected to be paratropic is more than halved, this overall 'London' (paramagnetic) contribution to the magnetic susceptibility of pyracylene, perpendicular to its molecular plane, is drastically reduced — from -3.84 down to -0.74 (relative to benzene).

(iii) The Coupled-Hartree-Fock Calculations Based
on Fixed Resonance-Integrals

With the parametrisation described in §8.3, the coupled-Hartree-Fock computation by the method of Hall and Hardisson¹⁹² (based on a wave function with fixed resonance-integrals — method (3) of §8.3) yielded 99.24×10^{-6} cgs emu* as the absolute value for the 'mobile' π -electron contribution to the magnetic susceptibility of pyracylene, perpendicular to its molecular plane. Since the corresponding contribution to the magnetic susceptibility of benzene, on the same parametrisation, is¹⁷⁶ -30.53×10^{-6} cgs emu, the 'London' susceptibility of pyracylene, relative to benzene, is -3.25 (that is to say, the "ring currents" of pyracylene are predicted by this method to exhibit quite definitely an overall paramagnetism; in fact, the ratio $(\chi_{\perp}^{\pi \text{ London}}(\text{pyracylene}) / \chi_{\perp}^{\pi \text{ London}}(\text{benzene}))$ of -3.25 obtained here compares reasonably (to within ca. 15%) with the value of this same ratio (-3.83) arising from the 'topological' calculation (see §8.4(i)). This last result appears empirically to confirm an earlier remark of O'Sullivan and Hameka²⁴⁵ (made, however, with specific reference to predominantly diamagnetic, alternant hydrocarbons) that "...London's calculation is perhaps less accurate than Hall and Hardisson's..." but that when only the ratios of London's result are used, it seems likely that "these ratios are quite accurate". (We emphasise that this statement is quoted in the context of a non-iterative calculation in both cases; see §8.4(iv)).

* The program of Lazzeretti and Taddei¹⁷⁶ operates in "non-S.I." units. This need not, however, concern us here for we shall be almost exclusively discussing the values of various magnetic-properties as a ratio to the corresponding quantities calculated, by the same method, for benzene.

It is also possible that the susceptibility ratios obtained from the very crudest HMO-calculations, based on the London-McWeeny method,¹³² agree (perhaps fortuitously) so well with those from the more-sophisticated coupled-Hartree-Fock SCF-procedures precisely because the former calculation takes molecular topology into account in such a rudimentary way.* In one respect, the PPP-SCF wave-function may also be regarded as being a reflection of molecular topology (though, in fact, a more subjective one, since it requires more semi-empirical parameters) in the sense that the core-Hamiltonian matrix-elements of such a wave function are non-zero only for bonds and, on the assumptions made in this calculation, have a common value for all bonds (see §8.4(iv)).

The Hall-Hardisson calculation, as originally presented,¹⁹² does not make provision for breaking down the total $\chi_{\perp}^{\pi}$ London into terms associated with each individual-ring of the polycyclic system; the method due to Coulson, Gomes and the present author¹⁶² (described as method (5) in §8.3) does, however, allow such a partition and the calculation based on fixed resonance-integrals (method (5) in §8.3) gave rise to -2.16 and -0.20 (expressed relative to the benzene value) for the "integrated π -electron current-densities"¹⁶² associated with the five-membered and six-membered rings, respectively, of pyracylene.

* Davies^{214b} has stated the opinion that ".... the comparative success of London's method for aromatic hydrocarbons may be attributed to the dependence of the theoretical anisotropy on the square of the area of the rings in a molecule" and that "... any method that takes this into account is likely to give reasonable results for the ratio...." of a given calculated-anisotropy to that evaluated, by the same method, for benzene. We might also add that, at least for strongly paramagnetic systems of the type considered here, another important requirement for obtaining 'reasonable' ratios is the use of a π -electron wave-function that is iteratively self-consistent with respect to resonance integrals and calculated bond-lengths; (see §8.4(iv)).

Once again, therefore, the predictions based on the most simple-minded ("topological") HMO wave-function (-2.32 and -0.39 for the "ring currents" in pyracylene) seem to be confirmed, at least semi-quantitatively, by this apparently more-sophisticated calculation. In particular, both five-membered and six-membered rings are again predicted to be paratropic.

(iv) The Importance of Iteration
with Respect to Bond Length

In the preceding three sub-sections we have noted the superficially somewhat surprising result that the SCF-calculations on pyracylene which were not iterative with respect to bond lengths were in better agreement with the simple HMO-calculation than with the iterative $\beta\omega'\omega''$ one. In Table 8.4 are listed "ring-current" intensities, based on a $\beta\omega'\omega''$ HMO-calculation, for pyracylene (XXXVII) (transcribed from Table 8.3), as well as for acepleiadylene (XL) and dipleiadiene (XLI). From this table, it can be seen that $4n$ -peripheral dipleiadiene ($n=4$) follows much the same pattern as $4n$ -peripheral pyracylene ($n=3$) in that all its rings are expected to be paratropic, on the basis of a simple, non-iterative, 'topological' HMO-calculation (Table 8.2), and yet diatropism is predicted for its six-membered rings when an iterative $\beta\omega'\omega''$ wave-function is used. In fact, on the basis of such an iterative calculation, the diamagnetic "ring-current" intensities in the six-membered rings of pyracylene (XXXVII) and dipleiadiene (XLI) are very nearly equal at ca. $1/3$ of the benzene value, while the five-membered rings of (XXXVII), and the seven-membered rings of (XLI), bear paramagnetic "ring-current" of approximately the same order of magnitude as the diamagnetic one in benzene. The $[4n+2]$ -peripheral hydrocarbon acepleiadylene (XL), however, which was unambiguously diamagnetic according to the topological calculation (Table 8.2), is still predicted to be strongly diamagnetic,

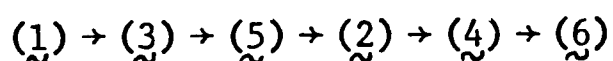
even by this iterative calculation; in fact, the "ring-current" intensity computed for its six-membered rings (ca. 1.20, on the basis of the $\beta\omega'\omega''$ wave-function) is almost the same as that (ca. 1.21) obtained via the topological calculation, although the diamagnetic "ring-current" intensities in the five- and seven-membered rings of (XLI) are predicted by the iterative calculation to be some 25% less than the corresponding 'topological' values.

Hence, it is seen that calculated "ring-currents" are much more sensitive to whether or not the wave function used to compute them is self-consistent with respect to atomic charges and bond orders in the case of overall paramagnetic, conjugated, π -electron systems than in the case of strongly diamagnetic ones. This is in fact not surprising, for paramagnetic contributions will be largest when magnetic dipole-transitions can take place between the ground-state (occupied) and excited-state (unoccupied) orbitals,^{19-25,110} and this activity will be particularly favoured when the separation between the highest-occupied (HOMO) and lowest-unoccupied (LUMO) orbitals is small. The smaller this separation turns out to be, however, the more likely is any estimated value of it to be sensitive to the idiosyncracies of the particular method used for the calculation. Hence, the predicted magnetic-properties of predominantly paramagnetic systems should be much more dependent upon the method used for their calculation than those of diamagnetic systems. In the latter cases, the diamagnetic contribution to the net current is the major one and this is a function only of the electron density in the ground state;^{19-25,110} any (relatively minor) paramagnetic-contribution which might possibly obtain is determined once again by the HOMO-LUMO separation which, in the case of diamagnetic systems, is much larger and estimates of it are, therefore, much less dependent on the peculiarities of the particular method used

to calculate it.

The above considerations are dramatically illustrated when the six different methods described in §8.3 are used to calculate the overall ratio $\chi_{\perp}^{\pi \text{ London}}(\text{molecule}) / \chi_{\perp}^{\pi \text{ London}}(\text{benzene})$, where $\chi_{\perp}^{\pi \text{ London}}(\text{benzene})$ is the 'London' contribution to $\chi_{\perp}^{\pi}$ calculated, by the same method, for benzene. Table 8.5 lists such calculations for our prototype molecule, pyracylene (XXXVII), and for its dianion (which is strongly diamagnetic — to about the same extent, in fact, as a condensed, benzenoid hydrocarbon of the same size^{*}). This Table illustrates the extreme sensitivity of the predicted magnetic-properties of predominantly paramagnetic, conjugated, π -electron systems to the method used for their calculation and the relative insensitivity in this respect of the predicted properties of ostensibly similar but predominantly dia-magnetic, conjugated species of this type.

Let us concentrate on pyracylene (XXXVII); as we proceed along the series



(where the numbers in brackets refer to the labellings of a particular computational-approach described in §8.3), we are progressing in what may be regarded as the direction of increasing sophistication of method, from the McWeeny approach¹³² based on a simple HMO (method (1)) to the formalism of Coulson et al.¹⁶² in the context of a coupled-Hartree-Fock method with variable resonance-integrals (method (6) of §8.3). Methods (1), (3) and (5) are all based on various types of wave functions which

* This therefore seems to illustrate an analogy, in the context of polycyclic "perturbed [4n]-annulenes", of Sondheimer's observation²⁷ that the dianions of genuine, mono-cyclic ("anti-aromatic") [4n]-annulenes are diamagnetic. This is certainly consistent with the large HOMO-LUMO separation (1.000 β) for (XXXVII)² predicted by the simple HMO-calculation.

are not self-consistent with respect to resonance integrals and calculated bond-orders, while methods (2), (4) and (6) are founded on the corresponding types of wave function which do incorporate such 'self-consistency'. It is clear, therefore, that the question of whether or not the wave function employed possesses such self-consistency is much more important, for the calculation of magnetic properties, than the question of whether that wave function is of the Huckel- or SCF-type — at least when the results are expressed as a ratio to the corresponding quantities ("ring-current" intensity or magnetic susceptibility) calculated, by the same method, for benzene. The ratio $\chi_{\perp}^{\pi \text{ London}}(\text{pyracylene}) / \chi_{\perp}^{\pi \text{ London}}(\text{benzene})$ obtained via method (1) is large and negative, indicating a strongly paramagnetic $\chi_{\perp}^{\pi \text{ London}}(\text{pyracylene})$; method (6), however, (as well as method (5)) predicts the London contribution to $\chi_{\perp}^{\pi}(\text{pyracylene})$ to be (marginally) diamagnetic; the other methods, (3), (5), (2) and (4), predict London susceptibility-ratios (in increasing order of diamagnetism) intermediate between these two extremes. It is evident, however, that the greatest discontinuity in the series occurs between methods (5) and (2) (separated by the dotted line in Table 8.5). It is in going from method (5) to method (2) that we change from using a wave function in which individual resonance-integrals are not self-consistent with respect to the corresponding calculated bond-orders to one in which these two quantities are self-consistent.

As for the dianion of pyracylene (XXXVII), all six methods agree that it should be strongly and unambiguously diamagnetic; all six methods predict London-susceptibility ratios which agree to within 15%. The dianion of pyracylene is, in fact, of some considerable interest for it does, of course, have the same carbon-atom connectivity and approximately the same ring-areas (the latter is not quite true but it is

assumed to be so in the present calculations) as the neutral molecule. To this level of approximation, therefore, the vast difference in magnetic behaviour between pyracylene and its dianion is a function mainly of electronic configuration (see for example, ref. 303). Once the assumption about invariance of molecular geometry between pyracylene and its dianion has been made in the context of the "topological" HMO-calculation (method (1)) and of those PPP-SCF calculations (methods (3) and (5)) which are not iteratively self-consistent with respect to resonance integrals and calculated bond-orders, such differences in magnetic behaviour are due only to electronic configuration; this is so because the wave function depends only on the carbon-atom connectivity of the system (e.g. §5.3), with the result that the π -electron energy-level family and the set of LCAO-coefficients of the various π -MO's are identical in the neutral molecule and in the dianion. Under these circumstances, the difference in calculated $\chi_{\perp}^{\pi}$ London between a given neutral-molecule and its dianion is attributable solely to the fact that the dianion has one more doubly-occupied orbital than the neutral molecule; there are thus consequential (and dramatic) changes in the HOMO-LUMO separation on which, according to Van Vleck's expression^{110,19}, the diamagnetic/paramagnetic nature of the species in question sensitively depends. This is certainly borne out by the figures presented in Table 8.5.

As a final emphasis of the message which is becoming clear from these calculations, we illustrate (in Table 8.6) the individual "ring-current" intensities in the five-membered and six-membered rings of pyracylene (XXXVII) and its diamagnetic dianion, calculated by the crudest (method (1) of §8.3) and the most-refined (method (6) of §8.3) approaches considered in this investigation. It is manifestly evident from these data that the relative currents in the dianion are hardly

changed when an SCF-method based on a wave function with variable resonance-integrals, and making minimal appeal to the London integral-approximation, is replaced by the McWeeny formalism founded on a simple Hückel-MO with fixed resonance-integrals. This is certainly not so for pyracylene itself, predicted by the simple Hückel-McWeeny method to be strongly paramagnetic. The results obtained by the more-refined calculation (method (6)) are even qualitatively different from those of the crudest (method (1)). In particular, the apparently paramagnetic "ring-current" noted in §8.4(i) as being borne by the six-membered ring in pyracylene is seen to be no more than an artifact of the simple 'topological' HMO-calculation based on fixed resonance-integrals.*

8.5 Conclusions

The following conclusions are drawn from the investigation presented in this chapter.

1. The calculated π -electron "ring-currents", "integrated current-densities" and 'London' contributions to magnetic susceptibilities of those molecules which a simple, non-iterative, Hückel-McWeeny calculation¹³² predicts to have an overall paramagnetic $\chi_{\perp}^{\pi}$ London, are extremely sensitive to the degree of sophistication of the method used to predict them. (See Tables 8.5 and 8.6).
2. In order for calculations on such systems to yield realistic results, it is vital that computations be based on a wave function that is

* Had this paramagnetic "ring-current" in the six-membered ring of pyracylene been genuine it would (to the author's knowledge) have been the first paramagnetic "ring-current" to be reported in a six-membered (i.e. formally 'benzenoid') ring. More-recent calculations by Gomes and the present author³⁵³ have, however, confirmed (by means of calculation by method (6) of §8.3) the notion of their being a paramagnetic "ring-current" in a six-membered ring in one of the isomers of pyracylene (dibenzo [cd,gh] pentalene) discussed by Trost and Kinson in ref. 361.

iteratively self-consistent with respect to resonance integrals and calculated bond-orders. Incorporation of this refinement is much more important than whether the wave function itself is chosen to be either of the Hückel- or SCF-type — at least when the results are expressed as a ratio to the corresponding quantities calculated, by the same method, for benzene. (Witness the results shown above and below the dotted line in Table 8.5.)

3. The calculated magnetic-properties of those conjugated systems which are predicted to have a strongly diamagnetic $\chi_{\perp}^{\pi}$ London are relatively insensitive to the idiosyncracies of the particular method used to calculate them (see Tables 8.5 and 8.6). When only ratios are required of "ring-current" intensities or 'London' contributions to magnetic susceptibilities (relative to the corresponding quantities calculated, by the same method, for benzene), it seems that for these strongly diamagnetic systems a calculation carried out by use of the simple McWeeny-method¹³² based on the crudest, non-iterative ("topological") Hückel-MO (method (1) of §8.3) is as adequate and as quantitative as either of the methods ((4) and (6)) which involve iterative, coupled-Hartree-Fock wave-functions.

4. The main lesson to be learned from these computations is that "ring-current" intensities calculated from simple Hückel- or even SCF-wave-functions that are not self-consistent with respect to resonance-integrals and calculated bond-length may be not merely quantitatively, but even qualitatively, very different from those estimated on the basis of the corresponding iterative-calculations. For example, of the present calculations, the "topological" (1) and "non-iterative" SCF ones ((3), (5)) favour the 'perturbed [4n]-annulene' model for pyracylene (Figure 8.1a) while the 'iterative' ones ((2), (4), (6)) point more to the 'naphthalene-core' model of Figure 8.1b. These observations evidently make the a priori prediction of the overall

(London) diamagnetic or paramagnetic nature of polycyclic hydrocarbons, merely by inspection, on the basis of their carbon-atom connectivity, a somewhat hazardous undertaking.*

* Conclusions 1-4 of this chapter have since been substantiated by a sequel to the above work, by Gomes and the present author,³⁵³ in which some isomers of pyracylene, previously discussed by Trost and Kinson,³⁶¹ were also subjected to the six different methods of calculation outlined in §8.3.

TABLE 8.1

π -Electron "Ring-Current" Intensities, from a Simple HMO-Calculation* (Method (1) of §8.3), in Molecules (XXXVII)-(XXXIX)

Compound	"Ring-Current" Intensity* in Rings			
	A	B	C	D
Pyracylene (XXXVII)	-0.38 ₆	-2.31 ₇		
1,2;5,6-Dibenzopyracylene (XXXVIII)	+0.57 ₁	-0.63 ₄	+0.56 ₃	
1,2-Diphenylpyracylene (XXXIX)	-0.26 ₃	-2.16 ₈	-2.02 ₈	+0.87 ₇

* Calculated from equations (3.33) and (6.15) and the assumptions detailed in the footnote on page 192 and expressed as a ratio to the diamagnetic "ring-current" intensity calculated, by the same method (see text), for benzene; a positive entry in the table therefore indicates a diamagnetic "ring-current", and a negative one, a paramagnetic "ring-current".

TABLE 8.2

π -Electron "Ring-Current" Intensities, via Method (1) of §8.3, in Pyracylene (XXXVII), Acepleiadylene (XL), Pyrene (VII) and Dipleiadiene (XLI)

Compound	"Ring-Current" Intensity* in Rings			
	A	B	C	
Pyracylene (XXXVII)	-0.38 ₆	-2.31 ₇		
Acepleiadylene (XL)	+1.20 ₇	+1.11 ₅	+1.17 ₀	
Pyrene (VII)**	+0.96 ₄	+1.32 ₇		
Dipleiadiene (XLI)	-0.70 ₀	-2.86 ₁		

* See footnote to Table 8.1
** Results for pyrene are taken from ref. 140.

TABLE 8.3

"Ring-Current" Intensities in Pyracylene (XXXVII) Calculated by
Methods (1)-(3) of §8.3.

Type of Calculation	"Ring-Current" Intensity in	
	Five-membered Rings (B)	Six-membered Rings (A)
London-McWeeny method based on a simple ('topo- logical') HMO (Method (1) of §8.3)*	-2.31 ₇	-0.38 ₆
London-McWeeny method based on an iterative ($\beta\omega'\omega''$) HMO (Method (2) of §8.3)**	-1.01 ₃	+0.30 ₈
Coupled-Hartree-Fock method based on a PPP-SCF wave function (Method (3) of §8.3)***	-2.15 ₆	-0.20 ₃

* See footnote to Table 8.1.

** Calculated from equations (3.33) and (6.15), the equations of Appendix D, and the assumptions detailed in the footnote on page 192, the imaginary bond-bond polarisabilities required having been computed from an iterative ($\beta\omega'\omega''$)-HMO, self-consistent with respect to charges and to bond orders.

*** The quantities listed here are those which, in ref. 162, are designated the relative "integrated π -electron current-densities" associated with a given ring.

TABLE 8.4

Relative π -Electron "Ring-Current" Intensities, Based on
an Iterative ($\beta\omega'\omega''$) HMO*, in Molecules (XXXVII), (XL) and (XLI)

Compound	"Ring-Current" Intensity* in Rings		
	A	B	C
Pyracylene (XXXVII)	+0.30 ₈	-1.01 ₃	+0.83 ₇
Acepleiadylene (XL)	+1.19 ₈	+0.81 ₈	
Dipleiadiene (XLI)	+0.34 ₄	-0.91 ₈	

* Via method (2) of §8.3; see the second footnote of Table 8.3, for details.

TABLE 8.5

'London' Contributions ($\chi_{\perp}^{\pi \text{ London}}(\text{species})/\chi_{\perp}^{\pi \text{ London}}(\text{benzene})$)
to Magnetic Susceptibilities Perpendicular to the Molecular
Planes of Pyracylene (XXXVII) and its Dianion, by Various Methods*

Method of Calculation	$(\chi_{\perp}^{\pi \text{ London}}(\text{species})/\chi_{\perp}^{\pi \text{ London}}(\text{benzene}))$	
	Pyracylene (XXXVII)	Pyracylene Dianion
Simple Hückel-McWeeny ¹³² (1) **	-3.84 [†]	+2.75 [†]
'Non-iterative' coupled- Hartree-Fock (Hall-Hardisson ¹⁹²) (3)	-3.25	+3.04
'Non-iterative' coupled- Hartree-Fock (Coulson-Gomes-Mallion ¹⁶²) (5) ----- ††	-2.93	+2.78
London-McWeeny ¹³² method based on an iterative ($\beta\omega'\omega''$)- HMO (2)	-0.73	-
Coupled Hartree-Fock (Hall-Hardisson ¹⁹²) with variable resonance-integrals (4)	+0.15	+2.85
Coupled Hartree-Fock (Coulson-Gomes-Mallion ¹⁶²) with variable resonance- integrals (6)	+0.31	+2.56

* Methods (1)-(6) of §8.3

** Numbers in brackets after the description of each method refer to the labelling of that method of calculation in §8.3, where further details may be found of the assumptions on which the computation in question is based.

† A negative value for the ratio ($\chi_{\perp}^{\pi \text{ London}}(\text{species})/\chi_{\perp}^{\pi \text{ London}}(\text{benzene})$) indicates a paramagnetic $\chi_{\perp}^{\pi \text{ London}}(\text{species})$; a positive value for the ratio indicates that $\chi_{\perp}^{\pi \text{ London}}(\text{species})$ is diamagnetic.

†† The dotted line divides the results from methods (1), (3) and (5) (which are all based on wave functions that are not iteratively self-consistent with respect to resonance integrals and calculated bond-orders) from the results obtained via methods (2), (4) and (6) which are based on wave functions which incorporate such 'self-consistency'.

TABLE 8.6

Relative* "Ring-Current" Intensities (by Method (1) of §8.3) and "Integrated π -Electron Current-Densities" (by Method (6)) in the Six-Membered (A) and Five-Membered (B) Rings of Pyracylene (XXXVII) and its Dianion

Method of Calculation	Pyracylene		Pyracylene Dianion	
	Relative* Currents in Rings		Relative* Currents in Rings	
	A	B	A	B
Method (1)** (McWeeny formalism ¹³² based on a simple, non-iterative HMO)	-0.39	-2.32	+0.61	+1.17
Method (6)** (Coulson-Gomes-Mallion formalism ¹⁶² , based on a PPP wave-function with variable resonance-integrals)	+0.57	-0.74	+0.66	+1.16

* Expressed as a ratio to the corresponding current calculated, by the same method, for benzene.

** For details of methods (1) and (6), see §8.3.

PART FIVE

GENERAL CONCLUSIONS

CHAPTER IX

GENERAL CONCLUSIONS TO THE WORK IN THIS THESIS:
THE PRESENT STATUS OF "RING-CURRENT" CALCULATIONS,
AND POSSIBLE FUTURE-DIRECTIONS IN THEIR USE.

As a result of the work described in this Thesis, and other contributions to the field over the last ten years, it is now becoming increasingly evident that use of the "ring-current" idea as a semi-quantitative, predictive tool in Theoretical Organic-Chemistry is presently at something of a watershed. On the one hand, if all that are required are calculations of relative, intra-molecular, "ring-current" ^1H -NMR chemical-shifts for the specially parametrised case of the condensed, benzenoid hydrocarbons, even the simplest and crudest "ring-current" theories may be used with considerable confidence, as Chapters II, III and VIII have indicated*. If, however, strongly paramagnetic systems are being dealt with, chemical-shift and magnetic-anisotropy predictions are much less reliable. Calculations on such systems will afford the possibility of realistic results only if they are based on a wave function that is iteratively self-consistent with respect to resonance integrals and calculated bond-orders. Chapter VIII has dramatically shown that incorporation of this latter refinement is much more important than the question of whether the wave function itself is chosen to be of the Hückel- or the SCF-type — at least when the results are expressed as a ratio to the corresponding quantities calculated, by the same method, for benzene. Furthermore, in the case of ^1H -NMR chemical-shift calculations on non-alternant hydrocarbons, even though Chapter VIII gives us reason to believe that the "ring-current" contributions to such shifts — in at least the diamagnetic molecules of this type — might be adequately estimated, there still remains the vexed question of the contribution which uneven charge-distribution

* Footnote on page 251.

makes to the ^1H -NMR shieldings in non-alternant molecules. This consideration is outside the scope of the present Thesis, but it is one which does merit further study for, in spite of some early work,^{212,293,205b,172a} the full, quantitative repercussions of this effect have not been convincingly substantiated.

As for the future, it is this author's considered opinion that there is not much further headway to be made in the domain of π -electron semi-empirical calculations (which have featured so prominently in this Thesis) and that the next phase which might possibly yield any dramatic progress of a quantitative and conceptual nature will be the application of ab-initio methods[†] to calculations of this type. Even though a formalism for gauge-invariant (Gaussian) atomic-orbitals in an ab-initio scheme is available²²¹, using it to calculate the magnetic properties of large, polycyclic, conjugated systems of the kind considered in this

* This statement has been vividly confirmed by some work which the author has completed since this Thesis was written: the ^1H -NMR data of refs. 60 and 174 were regressed against $\Delta\sigma/\Delta\sigma_{\text{benzene}}$ -ratios in which "ring-current" intensities were estimated quantum-mechanically (they were in fact the same as those used in Chapters II and III) but the geometric factors were calculated using the crudest-possible point-dipole approach, namely that due to Pople (ref. 6 and §1.3(v)(a)). The correlation coefficient obtained (0.97) was quite comparable with that found when the same experimental data were regressed against predictions of the Waugh-Fessenden-Johnson-Bovey theory (0.96 — Chapter II), the Biot-Savart method (0.98 — Chapter III), and the McWeeny approach based on a simple HMO wave-function¹⁴⁰ (0.96), and was better than that found when the calculated shifts were obtained via the McWeeny formalism based on uncoupled^{176a} (0.91) and coupled^{176b} (0.94) SCF-wave-functions. (It should, however, be mentioned that when the 'Bernstein, Pople and Schneider' assumption^{7,114,116a} of equal (unit) "ring-currents" in all rings was invoked, the correlation coefficient fell to only 0.81).

This somewhat salutary observation reinforces our previous conclusion (§8.5) that, when it comes to choosing a method to calculate the relative diamagnetic-properties of the condensed, benzenoid hydrocarbons, almost anything will do provided that the results are expressed as a ratio to the corresponding quantities calculated, by the same method, for benzene!

[†] Or, at least, all-valence-electron semi-empirical calculations.

Thesis is, as yet, not practicable[†]. One very worthwhile, and much needed, advance, which does lie in the context of semi-empirical calculations, would be the provision of a set of "ring-current" tables — analogous to those of Johnson and Bovey¹¹⁷ (§1.3(v)(b) and Chapter II) and the present author and Haigh¹³⁸ (§1.4(i)(j)), now routinely used by organic- and bio-chemists in the elucidation of molecular conformations — that are based on a quantum-mechanical method in which no appeal is made to the London integral-approximation (§§1.4(i)(e) and 1.4 (iii)). For although Chapters II and III have confirmed that intra-molecular "ring-current" effects on the ¹H-NMR shifts of the peripheral protons in condensed, benzenoid hydrocarbons (and, in particular, in benzene, on which "ring-current" shielding-tables are generally based), are well-predicted by even the simplest models when appropriately parametrised (§3.7), inter-molecular effects — particularly those on nuclei situated in the 'shielding cone' above the benzenoid ring, or in the ring plane and at some considerable distance from the ring centre — are by no means as reliably calculated (see §3.7 and refs. 304, 28, 38b, 138, 186 and 189). Therefore, until less-approximate semi-empirical tables, such as are described above, become available, those "ring-current" tables presently extant^{117,138} should be used in structural studies to provide evidence of only a corroboratory nature in cases where a molecular conformation has been almost unequivocally established by other physical means.* Indeed, those investigations in which numerical predictions of presently available "ring-current" tables^{117,138} have been used as the cornerstone of a

* This point has been developed in detail in the author's paper at the 11th Jerusalem Symposium on Quantum Chemistry and Biochemistry, which has recently been published (ref. 304).

† Considerable progress has, however, lately been made in more-rigorous calculations on smaller molecules; ref.231 gives a clear description of the methodology. Furthermore, changes in computer soft-wave and hard-ware observed over the last decade do perhaps caution against too categorical a statement that extensions of such calculations to larger molecules are necessarily far-distant.

conformational study are probably based on a disquietingly insecure foundation.

In the meantime, Chapters V, VI and VII (as well as Appendix C) have shown that there is indeed much interesting mathematics which underlies the "ring-current" concept, and it is perhaps fortunate that the intensive study of "ring-current" effects which has occurred in the last ten years has coincided with the realisation and exploitation, during the same period, of the essentially topological and graph-theoretical nature of simple molecular-orbital calculations on conjugated systems. This has by no means been a one-way process, for it has stimulated chemists (armed with the famous "chemist's intuition"!) to make contributions to areas of pure graph-theory — the work described in Appendix C is a prime example of this. Furthermore, as a consequence of preparing Chapters V-VII, the present writer has been led to other results in abstract graph-theory (which, however, are not reported in this Thesis since they do not have a direct bearing on "ring-current" ideas, though they have been published — see refs. 362, 314-316, 318, 304, 335, 310 and 331).

These topological ideas add to the value of the "ring-current" notion as an intuitive concept, for the organic chemist likes to think of "ring currents" as classical entities, and to regard an unsaturated, polycyclic hydrocarbon in the presence of an external magnetic-field as a kind of microscopic "Kirchhoff-network" (§6.3). Indeed, it is perhaps fitting that, over 100 years after his discussion of them, Kirchhoff's ideas³³⁷ on spanning trees (§6.3(v)) should find application, on a molecular scale, to problems ("ring currents" in conjugated systems) so analogous, superficially, to those (currents in a conducting network) which Kirchhoff himself considered³³⁷ on the macroscopic level (§6.3). This "ring-current" picture has proved itself, over the last 20 years,

to have great power in rationalising, at least qualitatively, the magnetic properties of π -electron systems; it is, furthermore, exceedingly pictorial so that one can, in a sense, almost "feel" what is happening when a large, conjugated molecule is subjected to an external magnetic-field. But of course, such a model is not, and never can be, accurate and, ultimately, for complete, quantitative reliability, an ab-initio formalism will have to be called upon. The irony here, however, is that, when this stage is reached, the sharp distinction on which the "ring-current" idea is firmly founded — namely, that of a σ - π separation — disappears; and, unfortunately, with this there also disappears the possibility of any simple, pictorial description of most of the characteristic experimental-features of the magnetic properties of conjugated systems discussed in this Thesis! Consequently, despite recent theoretical-advances described in this Thesis and elsewhere, and no matter what future refinements may be made to it, the "ring-current" idea seems destined, in the final analysis, to remain only a semi-empirical, semi-quantitative conceptual-aid. This is not, in any way, to deprecate the "ring-current" notion, nor to deny its aesthetic and practical utility, but is merely to place it in the context in which, by very definition, it belongs — namely, that of semi-empirical, π -electron theory.

* It should, however, be observed that provided that the calculation for a closed-shell system is not taken beyond the level of a single Slater-determinant, the current density (see §1.4(ii)(c)), like the expectation value of any other one-electron operator, can be expressed as a sum over occupied molecular-orbitals, and so, therefore, can the chemical-shift tensor. The contributions of σ - and π -electrons could thus in principle be distinguished (see, for example, Chapter 9 of ref.310). It seems likely, therefore, that a satisfactory, though arbitrary, distinction between local- and delocalised π -electron orbitals could be effected — though this would in practice presumably depend on the actual nature of the basis set.

A P P E N D I C E S

APPENDIX A

A CAVEAT ON INSERTION OF A TEST-DIPOLE CONTRIBUTION
 INTO THE VECTOR POTENTIAL APPEARING IN THE
 GAUGE FACTOR IN "RING-CURRENT" CALCULATIONS*

A1 Introduction

In §§3.1 - 3.3 and the remainder of Chapter III, considerable discussion was devoted to the legitimacy, or otherwise, of inserting a 'test'-dipole contribution into the vector potential appearing in the gauge factor in London's GIAO-scheme. It was concluded that, in the context of a semi-empirical formalism (which is what is primarily being considered in this Thesis), any illegitimacy involved in this procedure would simply be compensated for, numerically, by an appropriate empirical-parametrisation. In this Appendix, we briefly focus attention on the repercussions of this procedure, in the context of both exact and variational wave-functions.

A2 Chemical-Shift Calculations

In the presence of a vector potential $\underline{A}$, the one-electron Hamiltonian is

$$\mathcal{H} = \frac{1}{2m} (\underline{p} + e\underline{A})^2 + V \quad (A1)$$

We have the choice of defining $\underline{A}$ either by equation (3.2) (uniform field only) or via equation (3.3) (uniform field plus dipole field). With uniform field, $\underline{B}_0$, and dipole ($\underline{n}$) field in the

* I gladly acknowledge very helpful and exciting discussions with Professor S.T. Epstein, (University of Wisconsin, U.S.A.) — and, in particular, I am grateful for a personal communication from him dated December 10th, 1971 — concerning the material presented in this Appendix, which is included here by his kind permission.

Hamiltonian, the exact energy takes the form:

$$\begin{aligned} E &= E^{(00)} + B_0 \cdot E^{(10)} + n \cdot E^{(01)} \\ &+ n \cdot E^{(11)} \cdot B_0 + \frac{1}{2} B_0 \cdot E^{(20)} \cdot B_0 + \dots \end{aligned} \tag{A2}$$

where $E^{(\alpha \beta)}$ indicates the coefficient of a term which is α^{th} -order in B_0 and β^{th} -order in n . Evidently, therefore,

$$E^{(11)} = \left(\frac{\partial^2 E}{\partial n \partial B_0} \right)_{n = B_0 = 0} \tag{A3}$$

Furthermore, from equations analogous to (3.1)-(3.3), the wave function for the system will be dependent upon B_0 and n — i.e.

$$\Psi = \Psi(B_0, n) \tag{A4}$$

We now invoke the generalised Hellmann-Feynman Theorem^{363-366,137} to write (A3) in two different ways:

$$\begin{aligned} E^{(11)} &= \left(\frac{ \left(\frac{\partial}{\partial B_0} [\Psi(B_0, 0)], \frac{\partial H}{\partial n} \Psi(B_0, 0) \right) }{ (\Psi(B_0, 0), \Psi(B_0, 0)) } \right)_{\substack{B_0 = 0 \\ n = 0}} \end{aligned} \tag{A5}$$

and

$$\begin{aligned} E^{(11)} &= \left(\frac{ \left(\frac{\partial}{\partial n} [\Psi(0, n)], \frac{\partial H}{\partial B_0} \Psi(0, n) \right) }{ (\Psi(0, n), \Psi(0, n)) } \right)_{\substack{n = 0 \\ B_0 = 0}} \end{aligned} \tag{A6}$$

The expectation value on the right-hand side of (A5) is then the field, $\underline{B}'$, induced by $\underline{B}_0$ (with $\underline{n} = 0$), while that on the right-hand side of (A6) is the dipole moment, $\underline{m}$, induced by $\underline{n}$ (with $\underline{B}_0 = 0$) — i.e.

$$\underline{n} \cdot \underline{E}^{(11)}_{\underline{n}} \underline{B}_0 = \underline{n} \cdot \underline{B}' = \underline{m} \cdot \underline{B}_0 \quad (A7)$$

We thus have three equivalent procedures in the exact case:

- (A) Calculate $\underline{E}^{(11)}_{\underline{n}}$ directly
- (B) Calculate $\underline{B}'$
- (C) Calculate $\underline{m}$

Now, in a variational calculation, where we are not, any longer, dealing with exact wave-functions and energies — let us write $\Psi \rightarrow \hat{\Psi}$, $E \rightarrow \hat{E}$ — we can again carry through any of the procedures (A), (B) and (C), but the question which now arises is:- "Will they again all give the same result?" According to Hurley³⁶⁷, if the set of trial functions depends on $\underline{n}$, then almost certainly (A5) (with $\Psi \rightarrow \hat{\Psi}$, $E \rightarrow \hat{E}$) will not be true, and, if the set depends on $\underline{B}_0$, (A6) will not be true. In the case of a general, approximate wave-function, therefore, it seems that procedures (A), (B), and (C) will not necessarily lead to equivalent results.^{368,369}

A3 Application to Magnetic Susceptibilities

(An application of these considerations to the calculation of magnetic susceptibility is essentially formal, for in this case, there is, of course, really no need to introduce $\underline{n}$ at all!)

$$\underline{E}^{(20)}_{\underline{n}} = \left(\frac{\partial^2 E}{\partial \underline{B}_0 \partial \underline{B}_0} \right) \quad \begin{array}{l} \underline{B}_0 = 0 \\ \underline{n} = 0 \end{array} \quad (A8)$$

and the Hellmann-Feynman expression can be written:

$$\tilde{E}^{(20)} = \left(\frac{(\frac{\partial}{\partial \tilde{B}_0} [\Psi(\tilde{B}_0, 0)], \frac{\partial \mathcal{H}}{\partial \tilde{B}_0} \Psi(\tilde{B}_0, 0))}{(\Psi(\tilde{B}_0, 0), \Psi(\tilde{B}_0, 0))} \right)_{\substack{\tilde{B}_0 = 0 \\ (\tilde{n} = 0)}} \quad (A9),$$

the expectation value on the right-hand side being the dipole moment induced by $\tilde{B}_0$ (with $\tilde{n} = 0$); let us denote this by $\tilde{m}'$. The magnetic susceptibility may thus be calculated in two ways:

(A') Calculate $\tilde{E}^{(20)}$ directly

(B') Calculate $\tilde{m}'$ directly

Again, for an exact calculation, these will give rise to the same result. However, in an approximate, variational calculation, they will be expected to give rise to the same result only if the set of trial functions is independent of $\tilde{B}_0$ ³⁶⁷⁻³⁶⁹ — which is certainly not the case (cf. equation (3.1)) with the London set.

APPENDIX B

THE RÔLE OF LOCAL ANISOTROPIC-EFFECTS IN ^1H -NMR SHIELDING

During the course of this work, Barfield, Grant and Ikenberry published a very interesting and potentially significant paper¹²⁵ in which it was alleged that a considerable proportion of each proton-deshielding in the condensed, benzenoid hydrocarbons may be ascribed to anisotropic shielding-contributions at the carbon atoms, only the remaining 50% or less being attributed to "ring-current" effects. Following from the initial suggestion of Berthier et al.¹⁵¹ and using a crude estimate for the local paramagnetic-susceptibility in benzene, Pople^{370,242} had earlier estimated a contribution of almost 50% of the deshielding of the protons in benzene as being due to local anisotropic-effects. The novelty of the approach of Barfield et al.¹²⁵ is their use of modern experimental-values³⁷¹ of the carbon-13 tensor shielding-components for solid benzene, and they claim to show that local anisotropic-effects make substantial contributions to proton chemical-shifts for all condensed, benzenoid systems, and not just benzene. Until the advent of this paper, the established view (see refs. 8, 20, 111, 120, 122, 140, 170, 171, 176, 192, and many others) had been that chemical-shift contributions from the anisotropy in magnetic susceptibility of C-C and C-H σ -bonds vary very little between a benzene proton and protons in a general, polycyclic, benzenoid molecule, with the consequence that σ -bond anisotropies are not considered (see refs. listed above) to be important in determining the relative proton-chemical-shifts in such molecules, even though — as Pople^{370,242} and others³⁷² have shown — the absolute contribution from these effects may in fact be considerable. The paper of Barfield et al.¹²⁵ does, therefore, merit further examination and discussion.

In their approach, Barfield et al.¹²⁵ calculate the local-anisotropy contributions using a free-electron model (formally similar to equation (1.13) — but see ref. 125 for details) and the experimental results

of Pines et al.³⁷¹ They claim that this method (though it does in practice involve many assumptions, all detailed in ref. 125) makes use of no variable parameters, but "... the remainder [of the experimental shift], which must necessarily be determined empirically, is attributed to the delocalised (ring-current) effects."¹²⁵ They observe (though they admit that there seems to be no theoretical justification for the procedure) that if the local-anisotropy contributions to the ¹H-NMR shifts in condensed, benzenoid hydrocarbons are multiplied by a factor of two, an excellent empirical-correlation with the experimental data¹⁷⁴ is observed — thereby apparently obviating completely any need for a consideration of "ring-current" effects at all! The most remarkable feature of this correlation, however, is that it includes the sterically hindered protons, which are ordinarily omitted from comparisons of experimental and theoretical results since shifts due to London dispersion-forces arising from van-der-Waals interactions are expected to interfere in these situations (see §1.7, refs. 271-274, 120, 163, 170, 171, and 140 and §2.5(ii)). As the present author has pointed out to Barfield,³⁷³ for these sterically hindered protons there seems to be an approximately constant discrepancy (of, however, only ca. 0.1 ppm) between the experimental values and the local-anisotropy contributions multiplied by two; furthermore, in the unique case of proton 9 in 1, 2; 7,8 dibenzanthracene (compound (XV) of Figure 2.1), which is a doubly-overcrowded proton, this discrepancy seems to be approximately additive. It certainly is additive when just the "ring-current" contributions — parametrised to account entirely for the relative proton-chemical-shifts of the non-hindered protons, as in Chapters II and III and in refs. 120, 140, 170-172, 176, 218 — are subtracted from the experimental values (though in these cases the discrepancy is much greater — ca. 0.6 ppm). The experimental data reported by the present author and Haigh^{60,174} (used by Barfield et

al.¹²⁵) have now been subjected to comparison in this way with at least five different types of "ring-current" calculation:

- (i) the Hückel-McWeeny method¹⁴⁰; (ii) the Waugh-Fessenden-Johnson-Bovey approach,^{15,117} with relative "ring-current" intensities still determined by the Hückel-London-Pople-McWeeny¹³² procedure (Chapter II); (iii) a classical Biot-Savart formalism, again based on relative McWeeny "ring-current" intensities (Chapter III); (iv) the McWeeny method¹³² based on an uncoupled Hartree-Fock SCF wave-function^{176a}; (v) the McWeeny method¹³² based on a coupled Hartree-Fock wave-function.^{176b}

Within each of these five treatments, the discrepancy between "ring-current" predictions and experiment was approximately constant (at ca. 0.6 ppm) for singly-overcrowded protons ($H\alpha_3$ protons in Martin's terminology²⁴¹), and the discrepancy was nicely additive for the doubly-overcrowded proton in 1,2;7,8 dibenzanthracene (XV) (see, for example, §2.5(ii)). It is interesting, therefore, that by use of what Barfield et al.¹²⁵ admit is a somewhat 'magic' factor of two, their procedure can eliminate these overcrowded-proton discrepancies almost entirely — but only at the expense of virtually removing from consideration any "ring-current" contributions, even to the non-hindered protons! This would perhaps be acceptable were it not for the unfortunate paradox that, according to Barfield et al., it is necessary to invoke the idea of "ring-current" effects in order to rationalise the magnetic behaviour of the $(4n+2)$ -annulenes. As Barfield put it in a personal communication³⁷⁴ to the author: "It seems to me that [Grant's] initial intuition on this matter was that the local anisotropic contributions would dominate the aromatic shielding effects, but it was only later on that it became clear that the 'ring-current' effects were required to include effects of the annulenes as well."³⁷⁴

It appears, therefore, that the original hope of Barfield et al.¹²⁵

that local effects might be entirely dominant founders on exactly the same point as did Musher's similar proposal^{81,257} — i.e., accounting for the magnetic properties of the annulenes.²⁵⁹ This is not, however, to deny all substance to their suggestion that local anisotropic-effects might perhaps play a more-important rôle than we have accredited them in Chapters II and III of this Thesis — for, after all, by a judicious combination of calculated local-effects and empirically determined "ring-current" contributions, Barfield et al.¹²⁵ did achieve quite a reasonable correlation with the experimental proton-chemical-shifts¹⁷⁴; what the present author would point out here, however, is that Chapters II and III (supported by many published accounts — e.g. refs. 30, 120, 140, 163, 169-172, 176, 179, 203-205, 218) show that it is also possible to obtain empirical correlations with the same experimental data, of equal (or better) quality — as well as simultaneously to rationalise the observed magnetic-properties of the annulenes^{19-25,127,130,184} — by considering the "ring-current" effect alone. Furthermore, to the present writer, the latter procedure seems an aesthetically more satisfactory one than merely having to invoke the "ring-current" concept as a kind of ad-hominem after-thought when the local-anisotropy contributions are subsequently found to be inadequate to account for the observed magnetic-properties of the annulenes. In the final analysis, however, since we are working within the confines of a semi-empirical theory, these distinctions, and the particular approach adopted, are perhaps largely a matter of taste.

The author has suggested³⁷³ to Barfield that a set of related condensed, benzenoid hydrocarbons in which it would be most instructive to consider the interplay between local-anisotropic and "ring-current" effects are the helicenes; for previous work³⁵⁻⁴⁰ (including that involving the present author^{38,111}) indicates that chemical shifts in this series of molecules must to a certain extent rely for their

rationalisation on the postulate of some "ring-current" contributions, since the latter are likely to vary more rapidly than the local anisotropic-effects as a molecule is deformed from planarity. However, Barfield has replied³⁷⁴ that the local-anisotropy contributions out of the plane are thought to be substantial since (according to Barfield³⁷⁴) "there will be six terms from each carbon contributing." ³⁷⁴ It would, however, be necessary to calculate contours of such contributions at various heights above the plane and this is something which Barfield et al.^{125,374} have, as yet, not felt disposed to do. This might, however, be the subject of a future collaboration between the present author and Barfield.³⁷⁴

APPENDIX C

AN ELEMENTARY, NECESSARY CONDITION FOR HAMILTONIAN GRAPHS*

C 1 Introduction

It was emphasised in Chapter IX that the application of graph-theoretical techniques to this area of Physical Science is by no means a one-way process. Therefore, as an example of how consideration of the graph-theoretical aspects of "ring-current" calculations, and of Hückel theory in general (Chapters V-VIII), can inspire advances in pure Graph-Theory, we focus attention, in this Appendix, on the much-studied question of the conditions under which an arbitrary graph is Hamiltonian (see §5.2(iv) for definition).

C 2 Background

The determination of elegant necessary-and-sufficient conditions for a graph to be Hamiltonian is a well-known unsolved-problem in Graph Theory. Many sufficient conditions for a graph G to be Hamiltonian require G to have 'enough' edges; such results are due to Dirac³⁷⁵, Ore³⁷⁶, and Posa³⁷⁷, and to Chvátal³⁷⁸, who has extended all of them. It would, however, also be useful to have available some necessary conditions which might be applied to more-sparse graphs — that is to say, graphs (such as those which represent the carbon-atom connectivity of conjugated systems) which have a low edges-to-vertices ratio. For, just as a sufficient condition can give assurance that a given graph G is Hamiltonian, a necessary condition can guarantee that G is not

* The proofs detailed in this Appendix have been published. The full reference is:
F. HARARY and R.B. MALLION, "An Elementary, Necessary Condition for Hamiltonian Graphs, Involving Connectivity", Nanta Mathematica, 1974, Vol. 7, pp. 96 - 99.

The author acknowledges here and sets on record extensive collaboration with Professor Frank Harary (University of Michigan, U.S.A.) in the work reported in this Appendix. It is included in this Thesis with his kind permission.

Hamiltonian. Thus, when the graph whose Hamiltonicity is being investigated is not Hamiltonian, (as is often the case with molecular graphs), a necessary condition is rather more appropriate, as was seen in Chapter VI; sparse graphs are quite naturally encountered when the structures of polycyclic, conjugated hydrocarbons are represented graphically and, indeed, it was a consideration of the graph-theoretical aspects of "ring-current" calculations discussed in Chapter VI which led to the observations and theorems presented in this Appendix. Goodman and Hedetniemi³⁷⁹ have recently developed a sufficient condition for sparse graphs; our object here is to develop a necessary condition for a sparse graph G to be Hamiltonian.

C 3 Definitions

We first give some more graph-theoretical definitions, required for an understanding of the concepts specifically dealt with in this Appendix but not previously introduced in Chapter V. The new terms are underlined; all other graph-theoretical jargon, not otherwise explained here, is defined in §5.2.

A subgraph of a graph G is a graph having all of its vertices and edges in G . (See also p.166). For any set, T , of vertices of G , the induced subgraph, $\langle T \rangle$, is the maximal subgraph of G with vertex set T . If a graph G_1 has vertex set $V(G_1)$ and edge set $E(G_1)$, and $V(G_2)$ and $E(G_2)$ are similar quantities for a second graph G_2 , then the union, $G_1 \cup G_2$, is the graph with vertex set $V(G_1) \cup V(G_2)$ and with edge set $E(G_1) \cup E(G_2)$. The removal of a vertex v_i from a graph G results in that subgraph $G - v_i$ of G consisting of all vertices of G except v_i and all edges not incident with v_i . The removal of an edge x_j from G yields the spanning subgraph $G - x_j$ containing all edges of G except x_j . Some connected graphs can be disconnected by the removal of a single vertex, called a cutpoint. A cutpoint of a graph is a vertex whose

removal increases the number of components. A set S of vertices or edges — or vertices and edges — separates vertices u and v if u and v are in different components of $G - S$. The connectivity of a graph G is the smallest number of vertices which must be removed in order to disconnect G . A theta graph is a connected graph with two vertices of degree three connected by three disjoint paths of length at least two. If G is a graph in which the addition of a new edge e joining any two non-adjacent vertices always produces the same graph^{*}, then $G + e$ denotes that graph. If a bipartite graph G with m vertices in one set V_1 and with n vertices in the other set V_2 is such that every vertex of V_1 is joined by an edge to every vertex of V_2 , then G is called a complete bipartite-graph and is denoted $K_{m,n}$. Finally, a graph G with p vertices is pancyclic if it contains a cycle of every n , $3 \leq n \leq p$. A fortiori, every pancyclic graph is Hamiltonian.

C 4 Sufficient Conditions for a Graph to be Hamiltonian

Chronologically, the first such sufficient-condition for suitably dense graphs was due to Dirac³⁷⁵.

Condition 1. If G has $p \geq 4$ vertices, each of degree at least $p/2$, then G is Hamiltonian.

The next was due to Ore³⁷⁶.

Condition 2. If G has $p \geq 4$ vertices, and q edges, with $q > (p^2 - 3p + 6)/2$, then G is Hamiltonian.

Posa's condition³⁷⁷ was as follows:

Condition 3. Let G have $p \geq 3$ vertices. If, for every positive integer $n < (p-1)/2$, the number of vertices of degree at most n is less than n , and, furthermore, for odd p , the number of vertices of degree $(p-1)/2$ is at most $(p-1)/2$, then G is Hamiltonian.

Next, we consider a condition³⁰⁵ involving theta graphs (§ C3):

* Up to isomorphism — i.e. to within a relabelling of the vertices; (see the footnote on page 179).

Condition 4. Every non-Hamiltonian, two-connected graph has a theta subgraph.

We shall find the following condition, due to Chvátal³⁷⁸, useful in studying graphs of connectivity $\kappa \geq 2$.

Condition 5. If G is a connected graph having a set $S = \{u_1, u_2, \dots, u_n\}$ of vertices such that $G - S$ has more than n components, then G is not Hamiltonian.

A further excluded-subgraph result is due to Goodman and Hedetniemi³⁷⁹.

Condition 6. If G is two-connected and contains no induced-subgraph $\kappa_{1,3}$ or $\kappa_{1,3} + e$ (§C3), then G is Hamiltonian.

One of the most recent sufficient-conditions is the following theorem due to Bondy, Chvátal, Schmeichel and Hakimi³⁸⁰, concerning pancyclic graphs (§C3).

Condition 7. Let $d_1 \leq d_2 \leq \dots \leq d_p$ be the degree sequence of the graph G . If $d_k \leq k \leq p/2$ implies $d_{p-k} \geq p - k$, then p is pancyclic or bipartite; and if G is bipartite, it has a cycle of every length $2n$, $2 \leq n \leq p/2$.

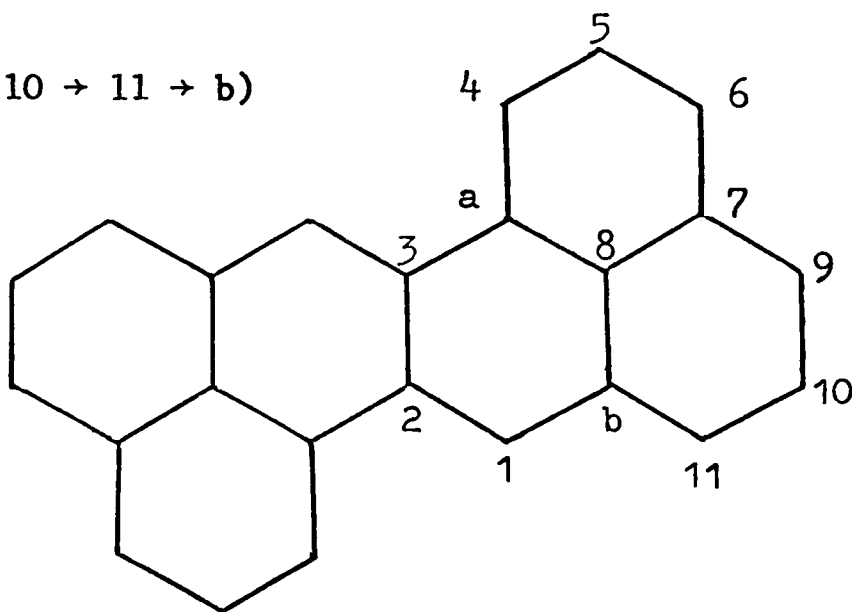
C 5 Inadequacy of Sufficient Conditions

As an example of the inadequacy of sufficient conditions for the Hamiltonicity of dense graphs, such as those outlined in §C4, let us consider the naphthalene molecular-graph. This has $p = 10$ vertices and, on Ore's condition (labelled '2' in §C4), an arbitrary connected-graph with 10 vertices would require $q \geq 38$ edges in order to be assured of being Hamiltonian. In fact, the naphthalene molecular-graph contains only $q = 11$ edges, and so would not be declared Hamiltonian on Ore's criterion (nor indeed on Posa's condition (No.3), nor on Dirac's corollary (Condition 1)). The naphthalene molecular-graph is, however, Hamiltonian, as is consistent with Theorem 2, given

below. The zethrene molecular-graph (Figure 6.6) has $p = 24$ vertices and would thus require $q \geq 255$ edges to be guaranteed its Hamiltonicity whereas it actually has only 29. This graph would thus not be declared Hamiltonian on conditions 1, 2 or 3. In fact, the zethrene molecular-graph is not Hamiltonian, as can be seen either from Theorem 2, below, or by noting that it contains two theta-subgraphs and is, therefore, non-Hamiltonian by Condition 4. (A theta subgraph in question is shown in Figure C1 in which points a and b are of degree 3 and are joined by paths

- 1) $a \rightarrow 8 \rightarrow b$
- 2) $a \rightarrow 3 \rightarrow 2 \rightarrow 1 \rightarrow b$
- 3) $a \rightarrow 4 \rightarrow 5 \rightarrow 6 \rightarrow 7 \rightarrow 9 \rightarrow 10 \rightarrow 11 \rightarrow b$

FIGURE C1



The zethrene molecular-graph is, however, path-Hamiltonian, as was observed in §6.4(iv) (Figure 6.6). As a final example, we may examine the molecular graph of decacyclene (Figure 6.2). This has $p = 36$ vertices and $q = 45$ edges but, with this number of vertices, would require $q \geq 591$ edges in order to be declared Hamiltonian on Ore's criterion (Condition 2)! Again, from Condition 1 or Theorem 2, below, this molecular graph is, in fact, non-Hamiltonian. As was noted in §6.3(iv), it is not even path-Hamiltonian (and, as a result, the Gayoso-Boucekkine¹⁶⁵ unitary-transformation was the only one which could be applied to the basis orbitals of this molecule, in the process of a "ring-current" calculation on it — see §6.3 (iii)).

From the above examples, it is quite evident that the conditions of Ore (Condition 2 of §C4), Posa (Condition 3) and the Corollary of Dirac (Condition 1) are much too weak to say anything useful about the Hamiltonian nature of the sorts of graphs which represent conjugated systems encountered chemically (that is to say, ones which have vertices only of degree three or less). Neither the naphthalene molecular-graph (which is Hamiltonian) nor that of zethrene (which is non Hamiltonian, but is path-Hamiltonian), nor the decacyclene molecular-graph (which is neither Hamiltonian nor path-Hamiltonian) would be declared Hamiltonian on these criteria — as indeed the latter two should not be; however, the Hamiltonicity of the naphthalene molecular-graph does go undetected by the criteria provided by Conditions 1 - 3.

In view of these considerations, therefore, we shall devote the remainder of this Appendix to the general problem of finding a necessary condition for a sparse graph to be Hamiltonian, by considering graphs of increasing connectivity. It will be seen that, after $\kappa = 3$, the approach proposed becomes somewhat unwieldy. This should not, however, cause concern for we have in mind application of the condition to particularly sparse graphs (such as molecular graphs), with relatively small connectivity.

C 6 Connectivity 1 and 2

We first recall the definitions of the terms Hamiltonian and path-Hamiltonian (§5.2(iv)) and formalise the idea of (u,v)-path-Hamiltonian. A graph G is Hamiltonian if it contains a spanning cycle; G is path-Hamiltonian if there exists at least one pair of distinct vertices between which there is a spanning path; and G is (u,v)-path-Hamiltonian if there is a spanning path joining the particular vertices u and v . Evidently, every Hamiltonian graph is also path-Hamiltonian.

Theorem 1. If G is Hamiltonian, then G is connected and has no cutpoints.

In particular, if G has connectivity 1 (so that G is connected and

FIGURE C 2

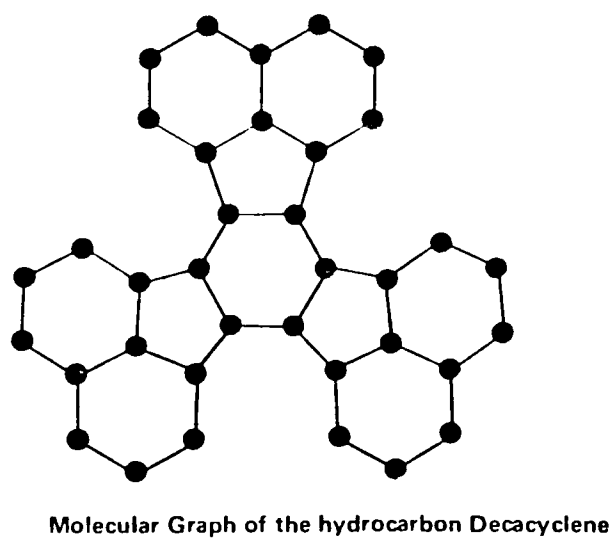
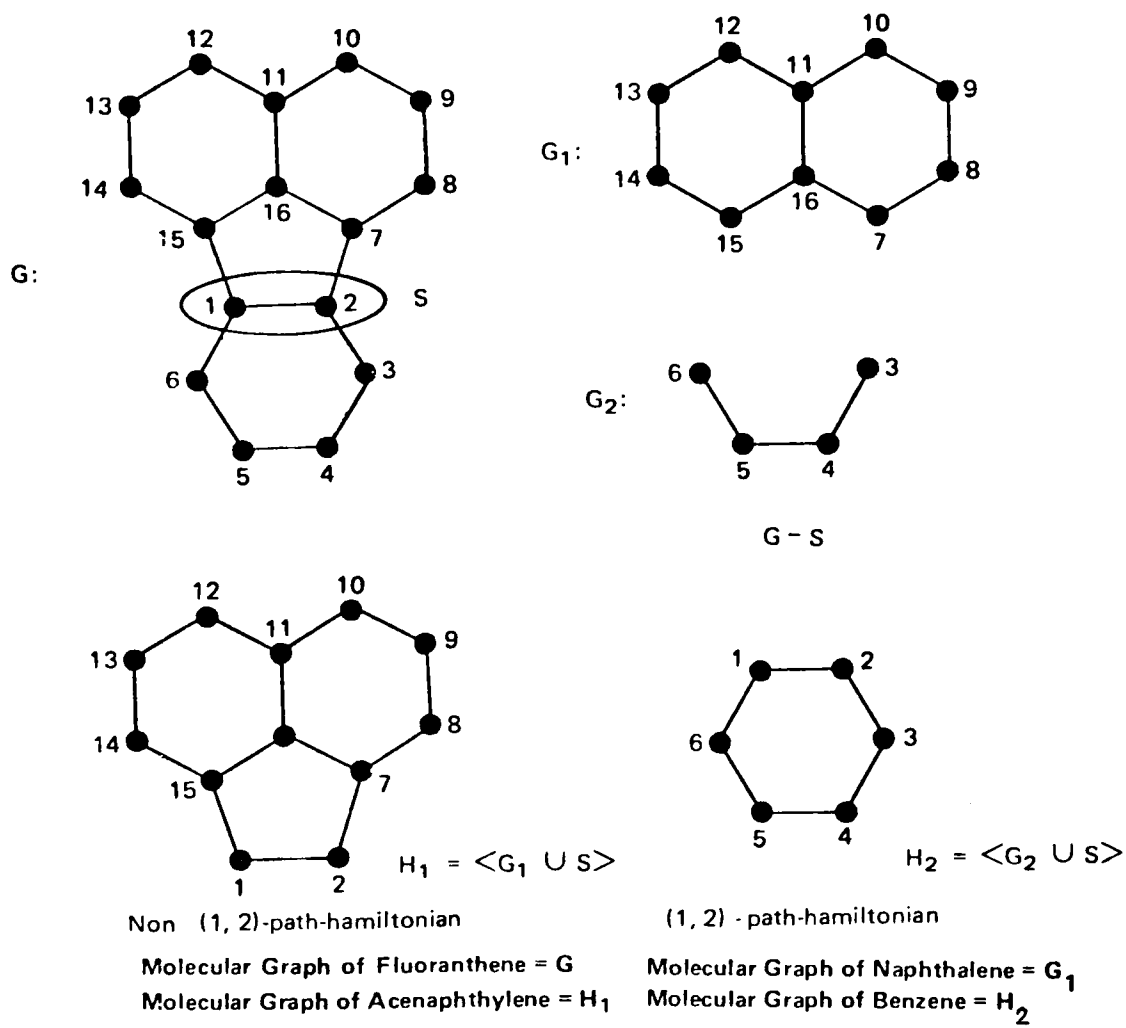


FIGURE C 3

has a cutpoint), then G is not Hamiltonian.

In view of Condition 5, on considering the case of a graph G of connectivity 2 with $S = \{u_1, u_2\}$ such that $G - S$ is not connected, we need confine our attention only to the case in which there are just two components of $G - S$.

Theorem 2. Let G have connectivity 2, with $S = \{u_1, u_2\}$ such that $G - S$ is not connected. Let there be just two components G_i , $i = 1, 2$, of $G - S$ and let H_i be the subgraph of G induced by $G_i \cup S$. Then, if G is Hamiltonian, both subgraphs H_i must be (u_1, u_2) -path-Hamiltonian.

Proof: By definition, any Hamiltonian cycle of G must encompass all the vertices of G_1 , of G_2 , and the vertices u_1 and u_2 , once, and once only. Such a Hamiltonian cycle must, therefore, leave G_2 and enter G_1 via u_1 and u_2 (or vice versa). We require that, during this process, all the vertices of G_1 shall have been visited and this is possible only if $\langle G_1 \cup S \rangle$ is (u_1, u_2) -path-Hamiltonian. Similarly, for G to be Hamiltonian it is necessary that H_2 also be (u_1, u_2) -path-Hamiltonian. Thus, if either of H_1 and H_2 is not (u_1, u_2) -path-Hamiltonian, then G cannot be Hamiltonian. Conversely, if G is Hamiltonian, then both H_1 and H_2 must be (u_1, u_2) -path-Hamiltonian, by means of the paths which follow a Hamiltonian cycle.

This theorem is illustrated by means of the examples shown in Figure C2. The graph depicted there represents the connectivity of the carbon atoms in fluoranthene (XX), and it is non-Hamiltonian (it is, however, path-Hamiltonian — for example, (10, 16)-path-Hamiltonian, on the labelling scheme adopted in Figure C2.) The molecular graph of fluoranthene constitutes a subgraph of that of decacyclene (see Figure C3) which (as was noted in §6.3(iv)) is not only non-Hamiltonian but is not, even, path-Hamiltonian.

FIGURE C 4

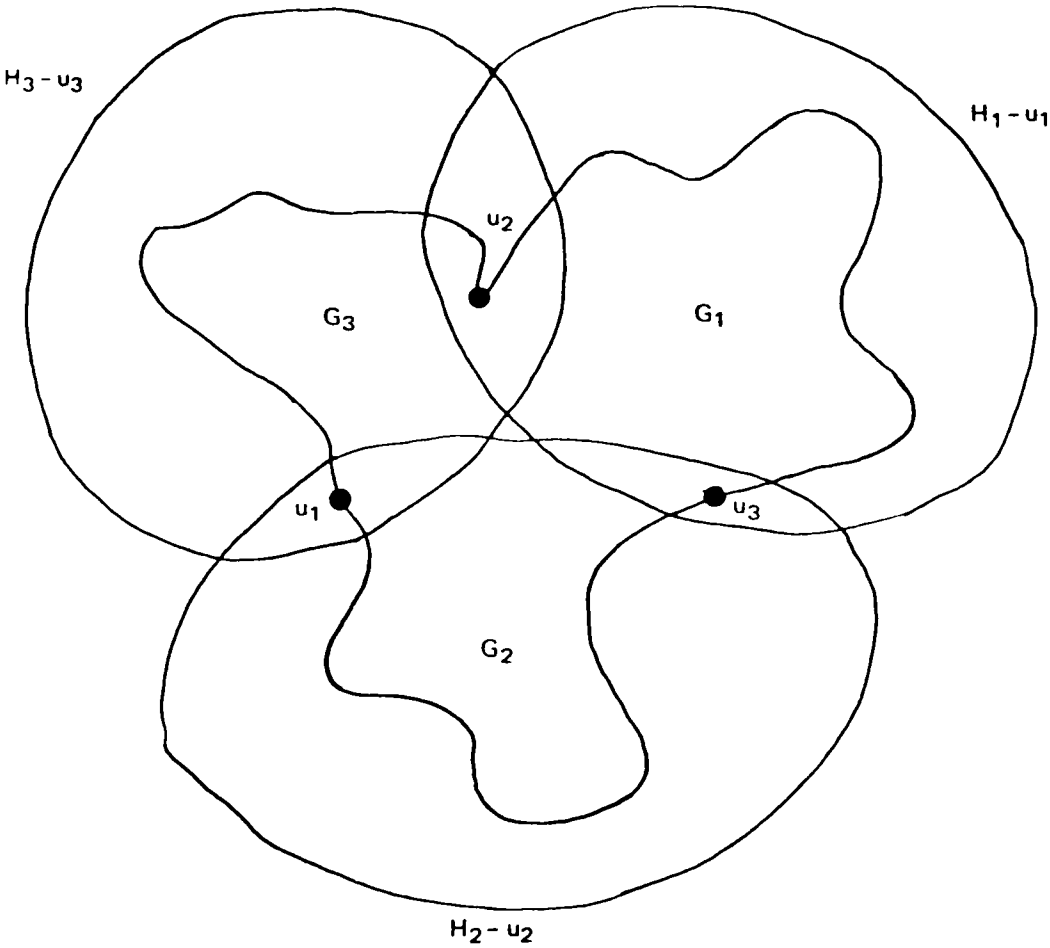
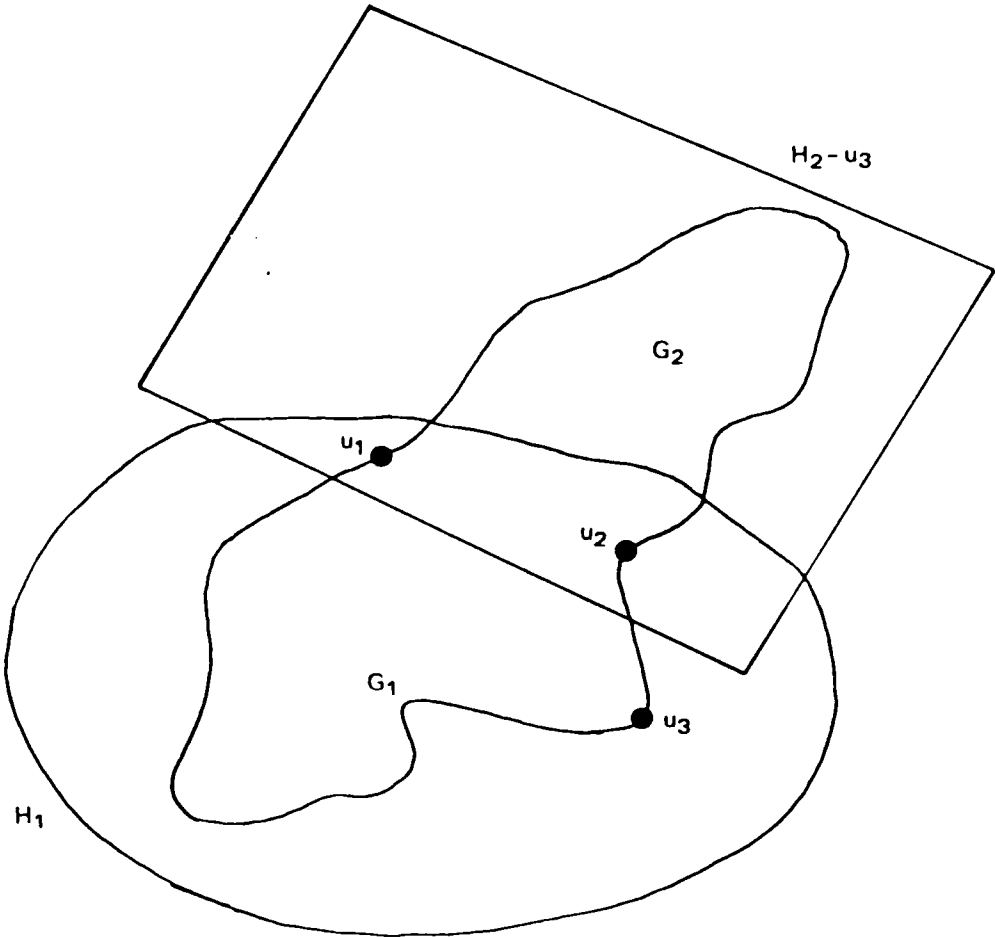


FIGURE C 5

C 7 Connectivity 3

Once more, in view of Condition 5, on considering the case of a graph G of connectivity 3 with $S = \{u_1, u_2, u_3\}$ such that $G - S$ is not connected, we need confine our attention only to the cases that $G - S$ has 2 or 3 components G_i , since, by Chvátal's Theorem, if $\kappa = 3$ and there are four components, then G is not Hamiltonian. It is necessary to discuss the spanning paths in more detail when S contains at least three vertices because they must involve different pairs of vertices of S .

Theorem 3. Let G have $\kappa = 3$ with $S = \{u_1, u_2, u_3\}$ such that $G - S$ is not connected; let G_i be the 2 or 3 components of $G - S$; and let $H_i = \langle G_i \cup S \rangle$.

(1) If there exist two components, G_i ; if G is Hamiltonian, then there exists a labelling of u_1, u_2, u_3 and an ordering of H_1 and H_2 such that H_1 and $(H_2 - u_3)$ are (u_1, u_2) -path-Hamiltonian.

(2) If there exist three components, G_i , of $G - S$, and G is Hamiltonian, then there exists a labelling of u_1, u_2, u_3 and an ordering H_1, H_2, H_3 such that each of the three subgraphs $(H_i - u_i)$ is (u_j, u_k) -path-Hamiltonian.

Proof* Case (1): $G - S$ has just 2 components (Figure C4).

Any Hamiltonian cycle of G must encompass all the vertices of G_1 and of G_2 , and the vertices u_1, u_2, u_3 just once. If there is some labelling such that H_1 and $(H_2 - u_3)$ are both (u_1, u_2) -path-Hamiltonian, then, clearly, G is Hamiltonian. The converse, in this context, follows from Theorem 2, thus settling the case of 2 components.

Case (2): $G - S$ has 3 components (Figure C5)

Again, a Hamiltonian cycle of G must take in all the vertices of G_1, G_2 and G_3 , and the vertices u_1, u_2, u_3 just once. Assume that there does exist a labelling of u_1, u_2, u_3 and an ordering H_1, H_2, H_3 of the

* This may be followed schematically with reference to Figures C4 and C5.

H_i such that $H_i - u_i$ is (u_j, u_k) -path-Hamiltonian, for the three cyclic permutations of $[i, j, k]$, starting from the permutation $[1, 2, 3]$.

Then, a path beginning at, say, u_2 could end at u_3 having taken in all the vertices of G_1 , since $(H_1 - u_1)$ (which comprises the vertices of $G_1 + u_2 + u_3$) is (u_2, u_3) -path-Hamiltonian. Similarly, a path starting at u_3 could end at u_1 having encompassed all the vertices of G_2 , since $(H_2 - u_2)$ (which comprises the vertices of $G_2 + u_3 + u_1$) is, by hypothesis, (u_3, u_1) -path-Hamiltonian. Finally, a path starting at u_1 could end at u_2 having taken in all the vertices of G_3 , since $(H_3 - u_3)$ (which comprises the vertices of $G_3 + u_1 + u_2$) is (u_1, u_2) -path-Hamiltonian. During the three stages of this process, the vertices visited are those of $(u_2 + G_1 + u_3)$, then $(u_3 + G_2 + u_1)$, then $(u_1 + G_3 + u_2)$ — that is to say, a Hamiltonian cycle has been traversed. If no such labelling exists (i.e. if any $(H_i - u_i)$ is not (u_j, u_k) -path-Hamiltonian), then G cannot be Hamiltonian.

C 8 Concluding Remarks

An extension of these observations to $\kappa = 4$ (where there is a possibility that G is Hamiltonian if $G - S$ has either 2, 3 or 4 components) may be accomplished, but the resulting theorems become too unwieldy to be of very general use. At this stage, therefore, when graphs of such a density are being considered, the earlier criteria applicable to non-sparse graphs (§C4) should, for preference, be invoked.

APPENDIX D

SOME TOPOLOGICAL* FORMULAE REQUIRED IN EQUATION (6.15)

We collect here some formulae for the topological* MO-quantities required in equation (6.15), since they do not appear to have been explicitly stated elsewhere[†] for the case of the non-alternant molecules, and, furthermore, the formula given originally by McWeeny¹³² as being applicable to the alternant hydrocarbons contains a misprint.

Firstly, let us call $\{x_I\}_{I=1,2,\dots,N}$ the eigenvalues of the molecular graph (that is to say, in the HMO-interpretation, $E_I = \alpha + x_I\beta$) and denote by the ordered set $\{c_{rI}\}_{r=1,2,\dots,N}$ the normalised eigenvector associated with the I^{th} eigenvalue; (see §§5.2(ii) and 5.3(i)). If any given eigenvalue of the adjacency matrix of the molecular graph (which, of course, has the properties of a real-symmetric matrix³⁸¹) is (say) m -fold degenerate, then appropriate linear-combinations must be taken of the m linearly independent eigenvectors all giving rise to this m -fold-degenerate eigenvalue, in such a way as to give m new eigenvectors which are mutually orthogonal; and a similar procedure must be adopted with the eigenvectors belonging to any other sets of degenerate eigenvalues which the spectrum of the molecular graph might contain. Secondly, we note that the Coulson-Rushbrooke 'starring' process¹⁰ is entirely equivalent (e.g. refs. 312, 313 and 310), graph theoretically, to a 'colouring' process,³⁰⁵⁻³⁰⁷ so that the molecular graphs of alternant hydrocarbons are what are known in graph-theoretical terminology as bipartite graphs, whilst those associated with non-alternant hydrocarbons are non-bipartite graphs. (Note, incidentally, that, for the simple, connected graphs we consider, which all have non-weighted vertices,³¹⁴⁻³¹⁸ all the diagonal elements of the real, symmetric, adjacency matrix $\mathbf{A}(G)$ are zero, and that, therefore — for both bipartite and non-bipartite molecular-graphs — $\sum_{I=1}^N x_I = \text{Tr } \mathbf{A} = 0$).

* But see ref. 303, p.165 of ref. 310, and §7.6 for a qualification of the use of the word "topological" in this context.

† Though this Appendix has now been published: for reference see footnote on page 169.

So far in this Appendix we have used only concepts associated with the adjacency matrix of the molecular graph. To be able to define the MO indices ($P_{(\omega)}$ and $\bar{\pi}_{(\omega)(\chi)}$) required in equation (6.15), however, we need to bring in the Aufbau process and Hund's rules (e.g. ref.20) in order to ascertain what, in MO-terminology, are called the 'orbital occupancies'; (in appropriate cases, however, even this procedure can be considered as an arbitrary, but purely topological, algorithm, as the present author and others have recently indicated in detail — see ref.303, p.165 of ref.310, and §7.6). The formulae which follow are applicable to closed-shell molecules—usually neutral species in which each atomic centre in the conjugated system contributes one electron*—with M doubly-occupied orbitals ($= \frac{1}{2}N$ for the even alternants we consider).

- i) $P_{(\omega)}$ terms: 'Topological' bond-orders for the cases outlined above have been well defined elsewhere (e.g. refs.139, 311d, 20 and 310); consequently, they are not reproduced here.
- ii) $\bar{\pi}_{(\omega)(\chi)}$ terms: Bond ω is defined from nucleus r of the conjugated system to nucleus s ($r \rightarrow s$) and χ is defined ($t \rightarrow u$) Notice that (cf. ref. 132) it is necessary to agree on an order for defining each bond (e.g. $r < s$) — though, of course, since this is a mutual polarisability, the order in which each bond is mentioned (e.g. (rs) before (tu)) is

* This will certainly, of course, always be so in the case of neutral hydrocarbons; when hetero-conjugated systems are considered, however, various situations can arise on the basis of the simple HMO-picture^{319,20,310} For example, a nitrogen atom in, say, pyridine^{180,341b} contributes (like a carbon atom) one electron to the system, and also constitutes one 'atomic centre' (i.e. vertex) in the molecular graph (actually it is what is called a weighted vertex of the graph — see refs. 314-318); an oxygen atom in a molecule such as furan constitutes one atomic centre, but is considered³¹⁹ to donate two electrons to the system. Even more-complex considerations arise when sulphur hetero-molecules are dealt with^{319,341a}.

immaterial¹¹¹ (see later — equation (D2)). Then,

$$\begin{aligned}\bar{\pi}(rs)(tu) &= \pi_{rs,tu} - \pi_{rs,ut} + \pi_{sr,ut} - \pi_{sr,tu} \\ & (= - \bar{\pi}(rs)(ut) = \bar{\pi}(sr)(ut))\end{aligned}\quad (D1)$$

where:

a) For non-alternant molecules (i.e. those with non-bipartite molecular-graphs)

$$\beta \bar{\pi}_{rs,tu} = 2 \sum_{I=1}^M \sum_{J=M+1}^N \frac{c_{rI} c_{sJ} c_{tJ} c_{uI}}{x_I - x_J} \quad (D2)$$

b) For alternant hydrocarbons (whose molecular graphs are bipartite) — and we here consider even ones — equations (D1) and (D2) can, of course, still be used to calculate $\bar{\pi}(rs)(tu)$ but, in this case, as McWeeny¹³² pointed out, by virtue of the Coulson-Rushbrooke 'pairing'-theorem¹⁰, the summations in equation (D2) can be confined entirely to the occupied (or unoccupied) MO's — i.e.

$$\beta \pi_{rs,tu} = 2 \sum_{I=1}^{\frac{1}{2}N} \sum_{J=1}^{\frac{1}{2}N} \frac{c_{rI} c_{sJ} c_{tJ} c_{uI}}{x_I + x_J} (-1)^{v_s + v_t} \quad (D3)$$

where $v_i = 1$ or 2 according to whether atom i is in the 'starred' or 'unstarred' set of vertices; (note that, in McWeeny's formula — equation (3.16) of his 1958 paper¹³² — the denominator is wrongly given as ' $x_I - x_J$ '). Also, in the case of alternant hydrocarbons:

$$\pi_{rs,ut} = \pi_{sr,tu} \quad (D4)$$

and so equation (D1) simplifies to:

$$\begin{aligned}\bar{\pi}(rs)(tu) &= 2(\pi_{rs,tu} - \pi_{rs,ut}) \\ & (= - \bar{\pi}(rs)(ut))\end{aligned}\quad (D5)$$

APPENDIX E

RELEVANT PAPERS PUBLISHED SINCE THE
THESIS WAS WRITTEN

As stated in the Preface, because of the writer's recent absence from Oxford, and current employment outside the academic sphere, this Thesis has been in production for a considerable period, during which time a few papers have been published which, had the opportunity been available, would have been referred to in Chapter I. In this Appendix, these papers are briefly reviewed, and their relation to work specifically reported in this Thesis is explained.

In a very thorough, and most interesting, investigation, Vos et al.³⁸² have studied "ring-current" effects in some heterocyclic anions related to anthracene and fluorene, via several approaches (including SCF-uncoupled- and coupled "ring-current" models). They have confirmed the conclusions reported in Chapter VIII (and in the 1976 paper with the late C.A. Coulson — referred to in the footnote on page 226 — on which that chapter was based) by stating that use of a coupled wave-function is mandatory for calculations on those systems which exhibit paramagnetic "ring-currents". Another of their conclusions is that the Johnson-Bovey^{15,117} model (§1.3(v)(b) and Chapter II), and quantum-mechanical methods based on what Roberts¹⁷⁷ describes as LAI (equation (1.118), page 78, §1.4(iii)), are superior in describing the "ring-current" effect. They conjecture whether this result can be generalised to other cyclic, conjugated systems, and they cite the present author's conclusion to Chapter III (published in the paper referred to in the footnote on page 114) that differences between the Biot-Savart model (Chapter III) and what is effectively the LA II-model¹⁷⁷ (equation (1.119), page 78, §1.4(iii)) are essentially absorbed in the parametrisation. These models do indeed also have a comparable quality in the treatment of Vos et al.³⁸², but these authors are of the opinion that the present

writer's conclusion seems not to be a general rule. Vos et al.³⁸² do, however, admit that ". . . . the use of charged systems to select an optimum ring-current model has appeared to be a seriously complicating factor."

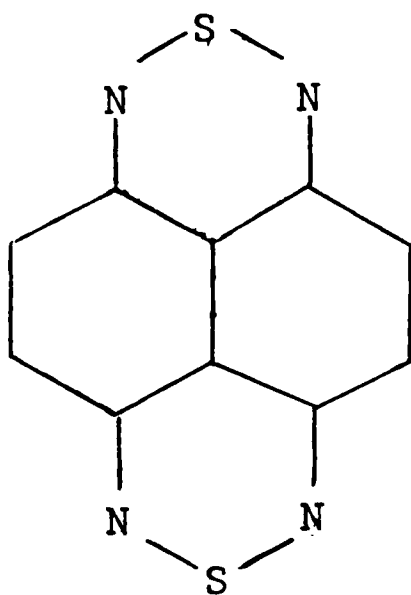
The "local-anisotropy" model of Barfield et al.¹²⁵ (a critique of which was given in Appendix B) has been applied by Agarwal et al.³⁸³ to calculate such contributions to the chemical shifts of protons sited above or near the conjugated rings of [10]-paracyclophane. The residual shift, not accounted for by the "local-anisotropy" effects, was shown to follow the Waugh-Fessenden-Johnson-Bovey model^{15,117}, but Agarwal et al.³⁸³ allege that the loop-separation originally invoked^{15,117} (§1.3(v)(b)) is unnecessary. These 'corrected' "ring-current" contributions were also shown by Agarwal et al.³⁸³ to give an excellent correlation with predictions of the Haigh-Mallion tables¹³⁸ (§1.4(i)(j)). They even managed to rationalise the now well-acknowledged fact^{38a,111,185-188,304,383,384} that the predictions of the Johnson-Bovey¹¹⁸ and Haigh-Mallion¹³⁸ tabulations differ by a factor of ca. 2.6 in the limit. Noting these observations, Agarwal et al.³⁸³ concluded: "It is especially gratifying to see that the two entirely different models are comparable with the experimental data. Previous statements that the two theories are only applicable to specific spatial regions of the aromatic molecule are nullified when the correct ring-current increments are evaluated. Thus, previously published experimental ring-currents which did not allow for the local anisotropic corrections would not be expected to fit either ring current model, except fortuitously."

Quite in contrast to this, however, Keller et al.,³⁸⁴ in another recent paper, have tested the Johnson-Bovey tables¹¹⁸ and the Haigh-

Mallion tables¹³⁸ (again on the cyclophanes!) and have come up with the more-conventional conclusion that ". . . the chemical shifts of the monitor protons (all of them being situated above and below the plane of the benzene ring considered) are consistent with shielding effects predicted by the classical theory . . . In contrast, the quantum-mechanical treatment considerably underestimates the shielding of protons in those regions.³⁸⁴" This is much more in line with previous beliefs on these matters.^{38a,111,185-188,304.}

Work on "ring-current" effects has now turned the full circle with the recent revival, by Abraham et al.,^{385,386} of the Pople point-dipole model (§1.3(v)(a)). The success which this group has achieved in applying that model to diamagnetic systems is by no means inconsistent with the present writer's long footnote on page 251. Classical models cannot, however, rationalise the properties of paramagnetic π -electron-systems, and interest in such species continues; Müllen has published³⁸⁷ some elegant experimental-work on the ^1H -NMR spectra of the dianions of pyrene (VII) and its isomers, regarded as "4n- π -perimeters." The ^1H -shifts of between 7.78 and 9.06 τ which Müllen observed in the dianion of pyrene (which are to be compared with a range of from 2.02 to 2.10 τ for the corresponding neutral-molecule) lend spectacular support to Sondheimer's observation which was discussed in the footnote on page 240 — itself confirmed by the calculations on the dianions of pyracylene, reported in Table 8.5. Subsequent (and, as yet, unpublished) calculations on the dianion of pyrene (VII), via methods (4) and (6) of §8.3, (carried out, at Müllen's behest,^{387b} by Gomes, Grossel and the present author) have confirmed the paramagnetic nature of the 'London' contribution from its π -electrons. Finally, Haddon et al.,³⁸⁸ recognising the intrinsic interest of the (as-yet-unsynthesised) molecule dipleiadiene ((XLI) — page 227) in the assessment of "ring-current" theories (see §§8.1 and 8.2 and the paper referred to in the footnote on page 226), have synthesised and

studied a sulphur-nitrogen heterocycle (XLII) which is iso- π -electronic with dipleiadiene (XLI); the molecule in question (XLII) contains two



(XLII)

- N S N - units which are each considered to donate four electrons to the π -system. The naphthalenic protons in (XLII) resonate at ca. 5.5τ , thus possibly confirming the suggestion of a paramagnetic "ring-current" indicated by a calculation (albeit an apparently non-iterative one) that Haddon et al.³⁸⁸ based on the Hückel-McWeeny formalism.¹³² Haddon et al.³⁸⁸ also maintain (as does the present author — see §8.4(iv) and the paper referred to in the footnote on page 226) that a calculated paramagnetic "ring-current" merely indicates the presence of a low-lying manifold of excited states, and that a given molecule cannot necessarily be declared to be "anti-aromatic" merely on that basis alone.

From this Appendix, it is evident that, despite the author's somewhat pessimistic stance concerning the future of semi-empirical π -electron calculations, adopted in Chapter IX, such calculations do still excite considerable interest in the Literature; it is clear, therefore, that the last word has by no means yet been said on the subject!

R E F E R E N C E S

REFERENCES

1. L. PAULING, J.Chem.Phys., 4, 673 (1936).
2. K. LONSDALE, Proc.Royal Soc., (London), A159, 149 (1937).
3. F. LONDON, (a) Comptes Rend. Acad.Sci. (Paris), 205, 28 (1937);
(b) J.Physique Radium, 8, 397 (1937);
(c) J.Chem.Phys., 5, 837 (1937).
4. J-F. LABARRE and F. CRASNIER, Fortschr.Chem.Forsch.: Topics in Current Chemistry, 24, 33 (1971).
5. L.H. MEYER, A SAIKA and H.S. GUTOWSKY, J.Amer.Chem.Soc., 75, 4567 (1953).
6. J.A. POPLÉ, J.Chem.Phys., 24, 1111 (1956).
7. H.J. BERNSTEIN, W.G. SCHNEIDER and J.A. POPLÉ, Proc.Royal Soc. (London), A236, 515 (1956).
8. K.D. BARTLE and D.W. JONES, in "Advances in Organic Chemistry" (Edited by E.C. Taylor), Vol 8, Wiley, London, United Kingdom, 1972: (a) p. 317; (b) Sec. IIIc pp. 383 and 422; (c) Sec. IV, pp. 385 and 423.
9. W.G. SCHNEIDER, H.J. BERNSTEIN and J.A. POPLÉ, J.Amer.Chem.Soc., 80, 3497 (1958).
10. C.A. COULSON and G.S. RUSHBROOKE, Proc.Cambridge Philos.Soc., 36, 193 (1940).
11. H.J. BERNSTEIN and W.G. SCHNEIDER, J.Chem.Phys., 24, 467 (1956).
12. W.G. SCHNEIDER, H.J. BERNSTEIN, and J.A. POPLÉ, (a) Canadian J. Chem. 35, 1487 (1957); (b) Annal.N.Y.Acad.Sci., 70, 806 (1958).
13. J.A. POPLÉ, W.G. SCHNEIDER and H.J. BERNSTEIN, "High Resolution Nuclear Magnetic Resonance", McGraw Hill, London, United Kingdom, 1959, p.268.
14. E.D. BECKER and R.B. BRADLEY, J.Chem.Phys., 31, 1413 (1959).
15. (a) J.S. WAUGH and R.W. FESSENDEN, J.Amer.Chem.Soc., 79, 846 (1957);
(b) J.S. WAUGH, ibid., 80, 6697 (1958).
16. B.H. SMITH, "Bridged Aromatic Compounds", Academic Press, London, United Kingdom, 1964.
17. J.R. LETO, F.A. COTTON and J.S. WAUGH, Nature, 180, 978 (1957).
18. L.M. JACKMAN, F. SONDHEIMER, Y. AMIEL, D.A. BEN-EFRAIM, Y. GAONI, R. WOLOVSKY and A.A. BOTHNER-BY, J.Amer.Chem.Soc., 84, 4307 (1962).

19. J.A. POPLE and K.G. UNTCH, J.Amer.Chem.Soc., 88, 4811 (1966).
20. L. SALEM, "Molecular Orbital Theory of Conjugated Systems", W.A. Benjamin, Inc., New York, United States of America, 1966, Chapter 4.
21. H.C. LONGUET-HIGGINS, Chem.Soc.Spec.Publ. No. 21, 109 (1967).
22. F. BAER, H. KUHN and W. REGEL, Z.Naturforsch., 22a, 103, (1967).
23. Y.G. DORFMAN, "Diamagnetism and the Chemical Bond", (Translation Editor: C.P. Poole), Elsevier, New York, United States of America, 1965, pp. 15,16.
24. T.K. REBANE, Acad.Sci.U.S.S.R., (a) 135, 46 (1960); (b) 135, 568 (1960).
25. R.C. HADDON, V.R. HADDON and L.M. JACKMAN, Fortschr.Chem.Forsch. : Topics in Current Chemistry, 16, 103 (1971).
26. P.J. GARRATT, "Aromaticity", McGraw Hill, London, United Kingdom, 1971, p.177.
27. F. SONDHEIMER, Accounts Chem.Research, 5, 81 (1972).
28. R.B. MALLION, "Nuclear Shielding", in Specialist Periodical Report on Nuclear Magnetic Resonance, Vol. 4 (Edited by R.K. Harris), The Chemical Society, London, United Kingdom, 1975, pp. 1-66.
29. B.M. TROST, G.M. BRIGHT, C. FRIHART, and D. BRITELLI, J.Amer.Chem.Soc., 93, 737 (1971).
30. H.P. FIGEYS, Chem.Comm., 1967, p. 495.
31. D.H. LO and M.A. WHITEHEAD, Chem.Comm., 1968, p.771.
32. H. YAMAGUCHI and T. NAKAJIMA, Bull.Chem.Soc. Japan, 44, 682 (1971).
33. (a) T. NAKAJIMA, Pure Applied Chem., 28, 219 (1971);
(b) T. NAKAJIMA and S. KOHDA, Bull.Chem.Soc. Japan, 39, 804 (1966).
34. J.L. ATWOOD, D.C. HRNCIR, C. WONG and W.W. PAUDLER, J.Amer.Chem.Soc., 96, 6132 (1974).
35. M.S. NEWMAN and D. LEDNICER, J.Amer.Chem.Soc., 78, 4765 (1956).
36. R.H. MARTIN, N. DEFAY, H.P. FIGEYS, M. FLAMMANG-BARBIEUX, J.P. COSYN, M. GELBCKE and J.J. SCHURTER, Tetrahedron, 25, 4985 (1969).
37. R.H. MARTIN, G. MORREN and J.J. SCHURTER, Tetrahedron Letters, 1969, p. 3597.
38. C.W. HAIGH and R.B. MALLION, (a) Molec.Phys., 22, 945 (1971);
(b) ibid., 22, 955 (1971).
39. H. WYNBERG, Accounts Chem. Research, 4, 65 (1971).

40. W.H. LAARHOVEN and R.J.F. NIVARD, Tetrahedron, 28, 1803 (1972).
41. A.J. JONES, Rev. Pure Applied Chem., 18, 253 (1968).
42. R.H. SARMA and R.J. MYNOTT, J.Chem.Soc.Chem.Comm., 1972, p. 975.
43. C.C. McDONALD and W.D. PHILLIPS, J.Amer.Chem.Soc., 89, 6336 (1967).
44. B. SHEARD and E.M. BRADBURY, Prog.Biophys.Molec.Biol., 20, 189 (1970).
45. A. ALLERHAND and E.A. TRULL, Ann.Rev.Phys.Chem., 21, 217 (1970).
46. O. JARDETSKY and N.G. WADE-JARDETSKY, Ann.Rev.Biochem., 40, 605 (1971).
47. A.D. BUCKINGHAM, T. SCHAEFER, and W.G. SCHNEIDER, J.Chem.Phys., 32, 1227 (1960).
48. J.V. HATTON and R.E. RICHARDS, Molec.Phys., 3, 253 (1960).
49. P. LASZLO, Prog. NMR Spectroscopy, 3, 231 (1967).
50. F.A.L. ANET and G.E. SCHENK, (a) J.Amer.Chem.Soc., 93, 556 (1971);
(b) ibid., 93, 3301 (1971).
51. G.P. SCHIEMENZ, J.Magn.Resonance, 6, 291 (1972).
52. O. JARDETSKY and N.G. WADE-JARDETSKY, J.Biol.Chem., 241, 85 (1966).
53. S.I. CHAN, B.W. BANGERTER, and H.H. PETER, Proc.Nat.Acad.Sci. U.S.A., 55, 720 (1966).
54. B.W. BANGERTER and S.I. CHAN, Biophysics, 6, 983 (1968).
55. S.I. CHAN and J.H. NELSON, J.Amer.Chem.Soc., 91, 168 (1969).
56. O. JARDETSKY and C.D. JARDETSKY, J.Amer.Chem.Soc., 82, 222 (1960).
57. R.J. ABRAHAM, R.A. BURBIDGE, A.H. JACKSON, and G.W. KENNER, Proc.Chem.Soc., 1963, p.134.
58. G.L. CLOSS, J.J. KATZ, F.C. PENNINGTON, M.R. THOMAS and H.H. STRAIN, J.Amer.Chem.Soc., 85, 3809 (1963).
59. C.W. HAIGH, M.H. PALMER and B. SEMPLE, J.Chem.Soc., 1965, p. 6004.
60. C.W. HAIGH and R.B. MALLION, J.Molec.Spectroscopy, 29, 478 (1969).
61. R.J. ABRAHAM, G.H. BARNETT, E.S. BRETSCHNEIDER and K.M. SMITH, Tetrahedron, 29, 553 (1973).
62. D.F. EWING, Organic Magn. Resonance, 5, 321 (1973).
63. K.D. BARTLE, R.B. MALLION, D.W. JONES and C.K. PICKLES, J. Phys. Chem., 78, 1330 (1974).

64. W.H. PIRKLE and S.D. BEARE, J.Amer.Chem.Soc., 91, 5150 (1969).
65. W.H. PIRKLE, R.H. MUNTZ and I.C. PAUL, J.Amer.Chem.Soc., 93, 2817 (1971).
66. (a) J.A. ELVIDGE and L.M. JACKMAN, J.Chem.Soc., 1961, p.859.
(b) J.A. ELVIDGE, Chem.Comm., 1965, p.160.
67. R. BRESLOW, Chem. & Eng.News, 43, 90 (1965).
68. E.D. BERGMAN and B. PULLMAN (Editors), "Jerusalem Symposium: Aromaticity, Pseudo-Aromaticity and Anti-Aromaticity", Israel Academy of Sciences and Humanities, Jerusalem, Israel, 1971.
69. Chemical Society Special Publication, No. 21, London, United Kingdom, 1967,
(a) H.C. LONGUET-HIGGINS, p. 109;
(b) E. VOGEL, p. 113;
(c) S. WINSTEIN, p.5.
70. M. OKI (Editor), "Sendai International Symposium: The Chemistry of Non-Benzenoid Aromatic Compounds", I.U.P.A.C. and Butterworths, London, United Kingdom, 1971.
71. G.M. BADGER, "Aromatic Character and Aromaticity", Cambridge University Press, Cambridge, United Kingdom, 1969.
72. H.J. DAUBEN, J.D. WILSON and J. LAITY, J.Amer.Chem.Soc., 91, 1991 (1969).
73. S. WINSTEIN, Quart.Rev., 23, 141 (1969).
74. C.D. POULTER, R.S. BOIKEN, J.I. BRAUMAN and S. WINSTEIN, J.Amer.Chem.Soc., 94, 2291 (1972).
75. S. FORSÉN and T. NORIN, Tetrahedron Letters, 1964, p.2845.
76. L.M. JACKMAN and S. STERNHELL, "Applications of N M R in Organic Chemistry", Pergamon Press, Oxford, United Kingdom, 1969, p. 94.
77. G.E. SCHENK and F.A.L. ANET, Tetrahedron Letters, 1971, p.2779.
78. J.E. ANDERSON, J.Chem.Soc. (B), 1971, p.2388.
79. W.W. SCHOELLER, Tetrahedron, 29, 929 (1973).
80. R.J. ABRAHAM, R.C. SHEPPARD, W.A. THOMAS and S. TURNER, Chem.Comm., 1965 p.43.
81. J.I. MUSER, (a) J.Chem.Phys., 43, 4081 (1965); (b) Adv.Magn. Resonance, 2, 177 (1966) (Appendix B).
82. D.E. JUNG, Tetrahedron, 25, 129 (1969).
83. E. CORRADI, P. LAZZERETTI and F. TADDEI, Molec.Phys., 26, 41 (1973).
84. R. BENASSI, P. LAZZERETTI and F. TADDEI, J.Phys.Chem., 79, 848 (1975).

85. R.H. LEVIN and J.D. ROBERTS, Tetrahedron Letters, 1973, p.135.
86. (a) T.D. ALGER, D.M. GRANT, and E.G. PAUL, J.Amer.Chem.Soc., 88, 5397 (1966); (b) A.J. JONES, P.D. GARDNER, D.M. GRANT, W.M. LITCHMAN and V. BOEKELHEIDE, J.Amer.Chem.Soc., 92, 2395 (1970).
87. A.J. JONES and D.M. GRANT, Chem.Comm., 1968, p. 1670.
88. R.J. ABRAHAM, G.E. HAWKES and K.M. SMITH, J.Chem.Soc. Perkin Trans. II, 1974, p.627.
89. (a) H. GÜNTHER and H. SCHMICKLER, Angew.Chem.Internat.Edn., 12, 243 (1973);
(b) H. GÜNTHER, H. SCHMICKLER, U.H. BRINKER, K. NACHTKAMP, J. WASSER and E. VOGEL, ibid., 12, 760 (1973).
90. P.W. SELWOOD, "Magneto Chemistry", (Second Edition), Interscience, New York, United States of America, 1956.
91. A. PULLMAN and B. PULLMAN, "Les Théories Électroniques de la Chimie Organique", Maçon, Paris, France, 1952, Chapter 9.
92. E.D. BERGMAN, J. HOARAU, A. PACAULT, A. PULLMAN and B. PULLMAN, J.Chim.Physique, 49, 474 (1952).
93. (a) J. HOARAU, Annal.Chim. (13^e Série), 1, 544 (1956);
(b) A. PACAULT, J. HOARAU, J. JOUSSOT-DUBIEN, B. LEMANCEAU, and N. LUMBROSO, "Proceedings of the 1957 Conference on Carbon", pp. 43-49, Pergamon Press, London, United Kingdom, 1958;
(c) J. HOARAU, J.Chim.Physique, 57, 885 (1960);
(d) L. CARALP, J. HOARAU and M. PESQUER, Comptes Rend.Acad.Sci. (Paris), C269, 480 (1969).
94. D.W. DAVIES, Nature, 190, 1102 (1961).
95. P. PASCAL, Annal.Chim. 19, 5 (1910).
96. W. HABERDITZL, Angew.Chem.Internat.Edn., 5, 288 (1966).
97. F. STENGER, Wied.Annal. (Annal.Physik) 20, 304 (1883) (Cited by S. MITRA in "Transition Metal Chemistry", Vol. 7 (Editor: R.L. Carlin), M. Dekker Inc., New York, United States of America, 1972, p.183).
98. C.V. RAMAN and K.S. KRISHNAN, Proc.Royal Soc. (London), A113, 511 (1927).
99. S. BHAGAVANTAM, Proc. Royal Soc. (London), A126, 143 (1929).
100. K.S. KRISHNAN, B.C. GUHA, and S. BANERJEE, Phil.Trans.Royal Soc. (London), A231, 235 (1933).
101. K.S. KRISHNAN and S. BANERJEE, Phil.Trans.Royal.Soc. (London), A234, 265 (1935).
102. K. LONSDALE and K.S. KRISHNAN, Proc.Royal Soc. (London), A 156, 597 (1936).
103. M. OWEN, Annal. Physik, 37, 657 (1912).

104. K. HONDA and T. SONÉ, Sci.Rep.Tôhoku Imperial University, Series I, 2, 25 (1913); (cited by Raman and Krishnan in ref. 98.)
105. C.V. RAMAN, Nature, (a) 123, 945 (1929); (b) 124, 412 (1929).
106. P.E. EHRENFEST, (a) Physica (Eindhoven), 5, 388 (1925); (b) Z.Physik, 58, 719 (1929).
107. A.R. UBBELOHDE, Nature, 132, 1002 (1933).
108. J. IBALL and J.M. ROBERTSON, Nature, 132, 750 (1933).
109. R. PEIERLS, Z.Physik, 80, 763 (1933).
110. J.H. VAN VLECK, "The Theory of Electric and Magnetic Susceptibilities", Oxford University Press, Oxford, United Kingdom, 1932.
111. R.B. MALLION, Ph.D. Thesis, University of Wales (U.C. Swansea), 1969.
112. J. HOARAU, N. LUMBROSO and A. PACAULT, Comptes Rend. Acad. Sci. (Paris), 242, 1702 (1956).
113. R.J. ABRAHAM, Molec.Phys., 4, 145 (1961).
114. I.J. MADDOX and R. McWEENY, J.Chem.Phys., 36, 2353 (1962).
115. E. HÜCKEL, Z. Physik, 76, 628 (1932).
116. J.D. MEMORY, (a) J.Chem.Phys., 38, 1341 (1963); (b) Biochim. Biophys.Acta, 66, 168 (1963).
117. C.E. JOHNSON and F.A. BOVEY, J.Chem.Phys., 29, 1012 (1958).
118. (a) J.W. EMSLEY, J.FEENEY and L.H. SUTCLIFFE, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, Oxford, United Kingdom, 1965, Appendix B.
(b) F.A. BOVEY, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, London, United Kingdom, and New York, United States of America, 1969, Appendix.
119. W.R. SMYTHE, "Static and Dynamic Electricity", McGraw Hill, Inc., New York, United States of America, 1939.
120. N. JONATHAN, S. GORDON and B.P. DAILEY, J.Chem.Phys., 36, 2442 (1962).
121. B.P. DAILEY, A. GAWER and W.C. NEIKAM, Discuss. Faraday Soc., 34, 18 (1962).
122. B.P. DAILEY, J.Chem.Phys., 41, 2304 (1964).
123. R.E. MAYO and J.H. GOLDSTEIN, Molec.Phys., 10, 301 (1965/1966).
124. N. KAMEZAWA, J.Magn.Resonance, 11, 88 (1973).
125. M. BARFIELD, D.M. GRANT and D. IKENBERRY, J.Amer.Chem.Soc., 97, 6956 (1975).
126. D.G. FARNUM and C.F. WILCOX, J.Amer.Chem.Soc., 89, 5379 (1967).

127. H.C. LONGUET-HIGGINS and L. SALEM, Proc. Royal Soc. (London) A257, 445 (1960).
128. F.W. SEARS, "Electricity and Magnetism" (Principles of Physics Series), Eleventh Printing, Addison Wesley Inc., Reading, United States of America, 1958, p.262.
129. C.A. COULSON, "Electricity", Fifth Edition, Oliver and Boyd, London and Edinburgh, United Kingdom, 1958, p. 104.
130. R.C. HADDON, Tetrahedron (a) 28, 3613 (1972); (b) 28, 3635 (1972).
131. J.A. POPLE, Molec. Phys. 1, 175 (1958).
132. R. McWEENY, Molec. Phys., 1, 311 (1958).
133. J.D. MEMORY, "Quantum Theory of Magnetic Resonance Parameters", McGraw Hill, New York, United States of America, 1968 (especially Chapters 5 and 6 and Appendices 5D and 6B).
134. D.E. O'REILLY, Prog. NMR Spectroscopy, 2, 1, (1967), (especially pp27-31).
135. R. McWEENY, Proc. Phys. Soc. A64, 261 (1951).
136. C.P. SLICHTER, "Principles of Magnetic Resonance", Harper, New York, United States of America, 1963, Chapter 4.
137. S.T. EPSTEIN, J. Chem. Phys., 58, 1592 (1973).
138. C.W. HAIGH and R.B. MALLION, Organic Magn. Resonance, 4, 203 (1972).
139. C.A. COULSON and H.C. LONGUET-HIGGINS, Proc. Royal Soc. (London), A191, 39 (1947).
140. C.W. HAIGH, R.B. MALLION and E.A.G. ARMOUR, Molec. Phys., 18, 751 (1970).
141. C.W. HAIGH and R.B. MALLION, Molec. Phys., 18, 767 (1970).
142. C.A. COULSON and S. SENENT, J. Chem. Soc., 1955, p.1819.
143. C.A. COULSON and C.W. HAIGH, Tetrahedron, 19, 527 (1963).
144. C.F. SQUIRE, Comptes Rend. Acad. Sci. (Paris), 206, 665 (1938).
145. M.G. EVANS, J. DE HEER, and J. GERGELY, Proc. Phys. Soc. A62, 505 (1949).
146. R. McWEENY, J. Chem. Phys., 17, 1341 (1949).
147. R. McWEENY, Proc. Phys. Soc., (a) A64, 921 (1951); (b) A65, 839 (1952); (c) A66, 714 (1953).
148. A. PULLMAN and G. BERTHIER, Comptes Rend. Acad. Sci. (Paris), 233, 1035 (1951).
149. E.D. BERGMAN, J. HOARAU, A. PACAULT, A. PULLMAN and B. PULLMAN, J. Chim. Physique (a) 48, 359 (1951); (b) 50, 176 (1953).

150. M. MAYOT, G. BERTHIER and B. PULLMAN, J. Physique Radium, (a) 12, 652, (1951); (b) 12, 717 (1951).
151. G. BERTHIER, M. MAYOT, A. PULLMAN and B. PULLMAN, J. Physique Radium, 13, 15 (1952).
152. R. PAUNCZ and F. BERENCZ, (a) Acta Chimica Acad. Sci. Hungarica, 2, 375 (1952); (b) Acta Physica Acad. Sci. Hungarica, 2, 183 (1952).
153. T.K. REBANE, (a) Doklady Akad. Nauk USSR, 114, 70 (1957); (b) "Stroenii Veshchestva i Spektroskopiya", Moscow, Soviet Union, 1959; (c) Vestnik Leningradskova Universita, 1963 (22), p.35.
154. (a) A. BOLOTIN, Lietuvos Fizikos Rinkinys, 1, 119 (1961); (b) C. RADVILAVICIUS, P. LUKOSIUS, and A. BOLOTIN, Lietuvos Fizikos Rinkinys, 2, 269 (1962).
155. T.B. COBB and J.D. MEMORY, J. Chem. Phys., 39, 2386 (1963).
156. C. RADVILAVICIUS and A.B. BOLOTIN, Lietuvos Fizikos Rinkinys, (a) 4, 358 (1964); (b) 5, 341 (1965); (c) 8, 159 (1968).
157. A. GOŁEBIEWSKI, J. NOWAKOWSKI and H. KOWALSKI, Acta Physica Polonica, 29, 195 (1966).
158. J. NOWAKOWSKI, Theoret. Chimica Acta (Berlin), 10, 79 (1968).
159. J.-P. CHAUSSE and J. HOARAU, J. Chim. Physique, 66, 1062 (1969).
160. A.T. AMOS and H.G.Ff. ROBERTS, Theoret. Chimica Acta (Berlin), 13, 421 (1969).
161. M. KUMANOVA and T.K. REBANE (a) Comptes Rend. Acad. Bulgare Sci., 23, 1051 (1970); (b) ibid., 24, 1007 (1971). (c) Vestnik Leningradskova Universitata, 1970 (4), p. 158.
162. C.A. COULSON, J.A.N.F. GOMES and R.B. MALLION, Molec. Phys., 30, 713 (1975).
163. H.P. FIGEYS, Tetrahedron Letters, 1966, p. 4625.
164. C.F. WILCOX, J.P. UETRECHT, G.D. GRANTHAM and K.G. GROHMANN, J. Amer. Chem. Soc., 97, 1914 (1975).
165. J. GAYOSO and A. BOUCEKKINE, Comptes Rend. Acad. Sci. (Paris), (a) C272, 184 (1971); (b) C274, 358 (1972).
166. H. YAMAGUCHI and T. NAKAJIMA, Bull. Chem. Soc. Japan, 47, 1898, (1974).
167. H. BROOKS, J. Chem. Phys., 9, 463 (1941).
168. G.W. WHELAND and S.L. MATLOW, Proc. Nat. Acad. Sci. U.S.A., 38, 364 (1952).
169. L. CARALP and J. HOARAU, J. Chim. Physique, 65, 1565 (1968).

170. J.D. MEMORY, G.W. PARKER and J.C. HALSEY, J.Chem.Phys., 45, 3567 (1966).
171. J.D. MEMORY and T.B. COBB, (a) J.Chem.Phys., 47, 2020 (1967); (b) Bull.Amer.Phys.Soc., 12, 132 (1967).
172. H.G.Ff. ROBERTS, Theoret.Chimica Acta (Berlin), (a) 15, 63 (1969); (b) 22, 105 (1971).
173. E.A.G. ARMOUR, B.Sc. Thesis, University of Edinburgh, 1964.
174. C.W. HAIGH and R.B. MALLION, Molec.Phys., 18, 737 (1970).
175. A.T. AMOS and H.G.Ff. ROBERTS, Molec.Phys., (a) 20, 1073 (1971); (b) 20, 1081 (1971); (c) 20, 1089 (1971).
176. P. LAZZERETTI and F. TADDEI, J.Chem.Soc. Faraday Trans. II, (a) 68, 839 (1972); (b) 68, 1825 (1972).
177. H.G.Ff. ROBERTS, Molec.Phys., 27, 843 (1974).
178. P. LAZZERETTI, Molec.Phys., 28, 1389 (1974).
179. G. EGE and H. VOGLER, Molec.Phys., 30, 1511 (1975).
180. A. VEILLARD, J.Chim.Physique, 59, 1056 (1962).
181. G. EGE and H. VOGLER, Z. Naturforsch. 27b, 1164 (1972).
182. E.J. VINCENT, R. PHAN-TAN-LUU and J. METZGER, Bull.Soc.Chim. France, 1966, p.3537.
183. G.W. PARKER and J.D. MEMORY, J.Chem.Phys., 43, 1388 (1965).
184. G. EGE and H. VOGLER, (a) Theoret.Chimica Acta (Berlin), 26, 55 (1972); (b) Z. Naturforsch. 27b, 918 (1972); (c) Theoret.Chimica Acta (Berlin), 35, 189 (1974).
185. H.L. CRESPI, J.R. NORVIS, J.P. BAYS, and J.J. KATZ, Annal.N.Y.Acad. Sci., 222, 800 (1973).
186. P.I. ROSE, Organic Magn. Resonance, 5, 187 (1973).
187. A.G. GONZALEZ, J.Chem.Soc. Perkin Trans. I, 1973, p.2637.
188. (a) T.L. JAMES. M.L. LUDWIG, and M. COHN, Proc.Nat.Acad.Sci. U.S.A., 70, 3292 (1973); (b) C.A. BROWNE, I.D. CAMPBELL, P.A. KIENER, D.C. PHILLIPS, S.G. WALEY and I.A. WILSON, J.Molec.Biol., 100, 319 (1976).
189. H.G.Ff. ROBERTS, Chem.Phys.Letters, 11, 259 (1971).
190. S. FUJII and S. SHIDA, Bull.Chem. Soc. Japan, 24, 242 (1951).
191. T. ITOH, K. OHNO and H. YOSHIKUNI, J.Phys.Soc.Japan, 10, 103 (1955).
192. G.G. HALL and A. HARDISSON, Proc. Royal Soc. (London), A268, 328 (1962).

193. T.G. EDWARDS and R. McWEENY, Chem.Phys.Letters, 10, 283 (1971).
194. A.T. AMOS and H.G.Ff. ROBERTS, J.Chem.Phys., 50, 2375 (1969).
195. (a) E. FEENBERG, Phys.Rev., 103, 1116 (1956);
(b) P. GOLDHAMMER and E. FEENBERG, ibid., 101, 1233 (1956).
196. (a) A.T. AMOS and J.I. MUSER, Molec.Phys., 13, 509 (1967);
(b) J.M. SCHULMAN and J.I. MUSER, J.Chem.Phys., 49, 4845 (1968).
197. A.T. AMOS, J.Chem.Phys., 52, 603 (1970).
198. H.G.Ff. ROBERTS, Theoret.Chimica Acta (Berlin), 33, 269 (1974).
199. A.J. SADLEJ, Personal Communication, July, 1976.
200. B.L. BURROWS, Internat.J.Quantum Chem., 7, 344 (1973).
201. R. PARISER and R.G. PARR, J.Chem.Phys. (a) 21, 466 (1953);
(b) 21, 767 (1953).
202. J.A. POPLI, Trans. Faraday Soc., 49, 1375 (1953).
203. L. CARALP and J. HOARAU, J.Chim.Physique (a) 60, 884 (1963);
(b) 65, 2104 (1968); (c) 66, 642 (1969); (d) 67, 624 (1970);
(e) 68, 63 (1971); (f) 69, 775 (1972).
204. G.G. HALL, A. HARDISSON and L.M. JACKMAN, Tetrahedron, 19 (Supplement 2), 101 (1963).
205. P.J. BLACK, R.D. BROWN and M.L. HEFFERNAN, Austral.J.Chem., 20, 1305 (1967).
206. C. GIESSNER-PRETTRE and B. PULLMAN, (a) Comptes Rend.Acad.Sci.(Paris), D266, 933 (1968); (b) ibid., D268, 1115 (1969); (c) J.Theoret.Biol., 27, 87 (1970); (d) ibid., 27, 341 (1970).
207. Y. MIKAMI, S. MIYAI, and T. NAKAJIMA, Bull.Chem.Soc. Japan, 46, 787 (1973).
208. H. SPIESECKE and W.G. SCHNEIDER, J.Chem.Phys., 35, 731 (1961).
209. Y.B. VYSOTSKII, J.Struct.Chem., 13, 462 (1972).
210. W.T. RAYNES, "Nuclear Shielding", in Specialist Periodical Report on Nuclear Magnetic Resonance, Vol. 3, (Edited by R.K. Harris), The Chemical Society, London, United Kingdom, 1974, pp.1-49, (especially pp.25,26.).
211. H.G.Ff. ROBERTS, Theoret.Chimica Acta (Berlin), (a) 17, 151 (1970);
(b) 22, 105 (1971).
212. P. LAZZERETTI and F. TADDEI, Molec.Phys., 22, 941 (1971).
213. D.W. DAVIES, Chem.Comm., 1965, p.258.
214. D.W. DAVIES, Trans.Faraday Soc., (a) 56, 1713 (1960); (b) 57, 2081 (1961).

215. D.W. DAVIES, Molec.Phys., 27, 1437 (1974).
216. P. LAZZERETTI and F. TADDEI, Molec.Phys., 27, 1439 (1974).
217. H.G.Ff. ROBERTS, Molec.Phys., 29, 1277 (1975).
218. E.R. LONG and J.D.MEMORY, (a) J.Chem.Phys., 61, 3865 (1974); (b) ibid., 65, 2918 (1976)
219. R. McWEENY, Chem.Phys.Letters, 9, 341 (1971).
220. (a) H.G.Ff. ROBERTS, Personal Communication, 1974;
(b) P. LAZZERETTI, Personal Communication, 1974.
221. G.G. HALL, Internat.J.Quantum Chem., 7, 15 (1973).
222. W.N. LIPSCOMB, in "Theoretical Chemistry" (Editor: W. Byers-Brown), Butterworths, London, United Kingdom, 1972, p.167.
223. (a) R.M. STEVENS, R.M. PITZER, and W.N. LIPSCOMB, J.Chem.Phys., 38, 550 (1963);
(b) R.M. STEVENS, E. SWITKES, E.A. LAWS, and W.N. LIPSCOMB, J.Amer.Chem.Soc., 93, 2603 (1971).
224. A.J. SADŁEJ and W.T. RAYNES, Chem.Phys., 7, 383 (1975).
225. R. DITCHFIELD, J.Chem.Phys., 56, 5688 (1972).
226. J.A.N.F. GOMES and R.B. MALLION, Unpublished Calculations, 1974.
227. A.J. SADŁEJ, Acta Physica Polonica, A49, 667 (1976).
228. H.F. HAMEKA, "Advanced Quantum Chemistry", Addison-Wesley, Cambridge, United States of America, 1965.
229. R. DITCHFIELD, Molec.Phys., 27, 789 (1974).
230. A.J. SADŁEJ, Chem.Phys.Letters, 36, 129 (1975).
231. K. THOMSEN and P. SWANSTRÖM, Molec.Phys., 26, 751 (1973).
232. P.W. SWANSTRÖM, W.P. KRAEMER and G.H.F. DIERCKSEN, Theoret. Chimica Acta (Berlin), 44, 109 (1977).
233. L.WEISENTHAL and A.M. de GRAAF, (a) Phys.Rev.Letters, 27, 470 (1971);
(b) J.Chem.Phys., 58, 249 (1973).
234. R.E. MOSS and A.J. PERRY, Molec.Phys., 23, 957 (1972).
235. R.G. WOOLLEY and J.E. CORDLE, Chem.Phys.Letters, 22, 411 (1973).
236. J.A.N.F. GOMES, (a) Personal Communication, 1973; (b) D.Phil. Thesis, University of Oxford, 1976.
237. G. DIERCKSEN and R. McWEENY, J.Chem.Phys., 44, 3554 (1966).
238. R. McWEENY, Chem.Phys.Letters, 1, 567 (1968).
239. M. GOEPPERT-MAYER and A.L. SKLAR, J.Chem.Phys., 6, 645 (1938).

240. D.W. DAVIES, "The Theory of Electric and Magnetic Properties of Molecules", J.Wiley, New York, United States of America, 1967.
241. R.H. MARTIN, Tetrahedron, 20, 897 (1964).
242. J.A. POPLER, J.Chem.Phys., 41, 2559 (1964).
243. H. BROOKS, J.Chem.Phys., 8, 939 (1940).
244. J.H. Van VLECK and A SHERMAN, Rev.Mod.Phys., 7, 167 (1935).
245. P.S. O'SULLIVAN and H.F. HAMEKA, J.Amer.Chem.Soc., 92, 1821 (1970).
246. J.R. PLATT, J.Chem.Phys., 17, 484 (1949).
247. K. RUEDENBERG and C.W. SCHERR, J.Chem.Phys., 21, 1565 (1953).
248. A.D. McLACHLAN and M.R. BAKER, Molec.Phys., 4, 255 (1961).
249. T.K. REBANE, Vestnik Leningradskova Universitata, (a) 1957, (10) p.11; (b) 1957, (16), p.19; (c) 1957, (22), p.70.
250. T.K. REBANE, Zh.Eksp.Teor.Fiz., 38, 963 (1960) [Soviet Physics - JETP], 11, 694 (1960) .
251. T.H. WALNUT, (a) Chem.Phys.Letters, 33, 596 (1975); (b) J.Chem.Phys., 64, 4531 (1976).
252. J. TILLIEU and J. GUY, Comptes Rend.Acad.Sci. (Paris), 239, 1203 (1954).
253. R.A. HEGSTROM and W.N. LIPSCOMB, Rev.Mod.Phys., 40, 354 (1968).
254. A.D. BUCKINGHAM and P.J. STILES, Molec.Phys., 24, 99 (1972).
255. P.J. STILES, (a) Molec.Phys., 27, 501, (1974); (b) Proc.Royal Soc. (London), A336, 251 (1974); (c) Personal Communication, 1975; (d) Chem.Phys.Letters, 30, 126 and 259 (1975); (e) Proc.Royal Soc. (London), A346, 209 (1975); (f) Molec.Phys., 29, 1271 (1975).
256. (a) P.J. STILES and R.M. WING, J.Magn.Resonance, 15, 510 (1974); (b) J.W. PERRAM and P.J. STILES, Proc.Royal Soc. (London), A349, 125 (1976).
257. J.I. MUSHER, J.Chem.Phys., 46, 1219 (1967).
258. H.F. HAMEKA, J.Chem.Phys., 37, 3008 (1962).
259. J.M. GAIDIS and R. WEST, J.Chem.Phys., 46, 1218 (1967).
260. J.A. POPLER, J.Chem.Phys., 37, 3009 (1962).
261. M.D. KUMANOVA and T.K. REBANE, Zh.Strukt.Khim., 12, 552 (1971). [J.Struct.Chem., 12, 507 (1971).]
262. J.I. MUSHER, Personal Communication, at York, 1970.
263. J.A. POPLER, (a) J.Chem.Phys., 37, 53 (1962); (b) Discuss. Faraday Soc., 34, 7 (1962).

264. A.F. FERGUSON and J.A. POPLE, J.Chem.Phys., 42, 1560 (1965).
265. S. GUHA and S. BASU, (a) Naturwiss., 45, 539 (1958); (b) ibid., 46, 317 (1959); (c) Chem.Listy, 60, 605 (1966).
266. H.J. DAUBEN, J.D. WILSON and J.L. LAITY, J.Amer.Chem.Soc., 90, 811 (1968).
267. G.W. SMITH, General Motors Report, 1960, p.317 (Cited in ref.261).
268. P.W. ATKINS and J.A.N.F. GOMES, Molec.Phys., 32, 1063 (1976).
269. K.D. BARTLE and J.A.S. SMITH, Spectrochimica Acta, 23A, 1689 (1967).
270. K.D. BARTLE and D.W. JONES, Trans.Faraday Soc., 63, 2869 (1967).
271. T.W. MARSHALL and J.A. POPLE, Molec.Phys., 3, 339 (1960).
272. T. YONEMOTO, Canadian J.Chem, 44, 223 (1966).
273. C. REID, J.Molec.Spectroscopy, 1, 16 (1957).
274. B.V. CHENEY, J.Amer.Chem.Soc., 90, 5386 (1968).
275. D. MARYNICK and T. ONAK, J.Chem.Soc.A, 1969, p. 1797.
276. C.D. HODGMAN (Editor), "Handbook of Chemistry and Physics", 39th Edition, Chemical Rubber Publ.Co., Cleveland, United States of America, 1957, p. 227.
277. R.B. MALLION, Unpublished calculations, 1970.
278. M.A. COOPER and S.L. MANATT, J.Amer.Chem.Soc., 92, 1605 (1970).
279. J.A. POPLE, Proc.Royal Soc. (London), A239, 541 (1957).
280. C.W. HAIGH, Personal Communication, 1971.
281. R. McWEENY and B.T. SUTCLIFFE, "Methods of Molecular Quantum-Mechanics", Academic Press, London, United Kingdom, 1969, Appendix I, p. 266.
282. W.T. RAYNES, "Nuclear Shielding" in Specialist Periodical Report on Nuclear Magnetic-Resonance, Vol.1, (Edited by R.K. Harris), The Chemical Society, London, United Kingdom, 1972, Chapter 1, (especially pp.2-4).
283. J. KUTHAN, (a) Z.Chem., 6, 150 (1966);
(b) Collection Czech.Chem.Comm., 33, 1220 (1968);
(c) ibid., 35, 714 (1970).
284. J. KUTHAN, Personal Communication to R.B.M., November 5th, 1973.
285. J. KUTHAN and V. SKALA, Z.Chem., 6, 422 (1966).
286. J. KUTHAN, Z. DONNEROVA and V. SKALA, Collection Czech.Chem. Commun., 34, 2398 (1969).

287. B. CLIN and B. SALIER, Comptes Rend.Acad.Sci (Paris), D271, 858 (1970).
288. K.D. BARTLE and D.W. JONES, J.Phys.Chem., 73, 293 (1969).
289. F.L. HIRSHFELD, S. SANDLER, and G.M.J. SCHMIDT, J.Chem Soc, 1963, p.2108.
290. A.O. McINTOSH, J.M. ROBERTSON and V. VAND, J.Chem.Soc., 1954, p.1661.
291. I.R. MACKAY, J.M. ROBERTSON and J.G. SIME, Chem.Comm., 1969, 1470.
292. H. SPIESECKE and W.G. SCHNEIDER, Tetrahedron Letters, 1961, p.468.
293. T. SCHAEFER and W.G. SCHNEIDER, Canadian J.Chem., 41, 966 (1963).
294. C.A. COULSON and A. STREITWIESER, "Dictionary of π -Electron Calculations", Pergamon Press, London, United Kingdom, 1965.
295. C.A. COULSON, "Valence", Second Edition, Oxford University Press, London, United Kingdom, 1961, p.271.
296. M.J.S. DEWAR in R. DAUDEL (Editor), "The Applications of Wave-Mechanical Methods to the Study of Molecular Properties", Interscience Publishers Ltd., London, United Kingdom, 1965, p.65.
297. H.H. GREENWOOD and R. McWEENY, Advances in Phys.Org.Chem., 4, 73 (1966).
298. F. BURKITT, C.A. COULSON and H.C. LONGUET-HIGGINS, Trans. Faraday Soc., 47, 553 (1951).
299. M.R. SPIEGAL, "Statistics", McGraw-Hill, Inc., New York, United States of America, 1961, p.247.
300. K.D. BARTLE, Organic Magn.Resonance, 5, 95 (1973).
301. J. KUTHAN and T.M. KRYGOWSKI, Tetrahedron Letters, 1970, 4109.
302. M. KARPLUS and J.A. POPLE, J.Chem.Phys., 38, 2803 (1963).
303. R.B. MALLION and D.H. ROUVRAY, Molec.Phys., 36, 125 (1978).
304. R.B. MALLION, in "Nuclear-Magnetic-Resonance Spectroscopy in Molecular Biology" (Editor: B. Pullman) Reidel, Dordrecht, The Netherlands, 1978, pp. 183-191.
305. F. HARARY, "Graph Theory", Addison-Wesley, Reading, United States of America, 1969.
306. C. BERGE, "The Theory of Graphs", Methuen, London, United Kingdom, 1962.

307. R.J. WILSON, "Introduction to Graph Theory", Oliver and Boyd, Edinburgh, United Kingdom, and Academic Press, New York, United States of America, 1972.
308. M.J. RIGBY, Chemistry Part-II Thesis, University of Oxford (Department of Theoretical Chemistry), 1976.
309. A. CAYLEY, Phil.Trans.Royal Soc. (London), 148, 17 (1858) (esp. p. 20).
310. C.A. COULSON, B. O'LEARY and R.B. MALLION, "Hückel Theory for Organic Chemists", Academic Press, London, United Kingdom, 1978; esp. pp. 29-31 and Appendix A.
311. (a) K. RUEDENBERG, J.Chem.Phys., 22, 1878 (1954); (b) H.H. GUNTARD and H. PRIMAS, Helv.Chimica Acta, 39, 1645 (1956); (c) K. RUEDENBERG, J.Chem.Phys., 29, 1232 (1958); (d) K. RUEDENBERG, ibid., 34, 1881 and 1884 (1961); (e) H.H. SCHMIDTCKE, ibid., 45, 3920 (1966); (f) H.H. SCHMIDTCKE, Theoret.Chimica Acta (Berlin), 9, 199 (1968).
312. I. GUTMAN and N. TRINAJSTIĆ, Forschr.Chem.Forsch., Topics in Current Chemistry, 42, 49 (1973).
313. D.H. ROUVRAY, in "Chemical Applications of Graph Theory" (Editor: A.T. Balaban), Academic Press, London, United Kingdom, 1976, Chapter 7, Appendix I.
314. R.B. MALLION, N. TRINAJSTIĆ and A.J. SCHWENK, Z.Naturforsch., 29a, 1481 (1974).
315. R.B. MALLION, A.J. SCHWENK and N. TRINAJSTIĆ, Croatica Chemica Acta, 46, 171 (1974).
316. R.B. MALLION, A.J. SCHWENK and N. TRINAJSTIĆ, in "Recent Advances in Graph Theory": Proceedings of the Second Czechoslovak Symposium on Graph Theory (Editor: M. Fiedler), Academia, Prague, Czechoslovakia, 1975, pp.345-350.
317. A. GRAOVAC, O.E. POLANSKY, N. TRINAJSTIĆ, and N. TYUTYULKOV, Z.Naturforsch., 30a, 1696 (1975).
318. M.J. RIGBY, R.B. MALLION and A.C. DAY, Chem.Phys.Letters, (a) 51, 178 (1977); (b) 53, 418 (1978).
319. A. STREITWIESER, "Molecular-Orbital Theory for Organic Chemists", Wiley, New York, United States of America, 1961.
320. I. SAMUEL, Comptes Rend.Acad.Sci.(Paris), 229, 1236 (1949).
321. C.A. COULSON, Proc.Cambridge Philos.Soc. 46, 202 (1950).
322. R. GOUARNÉ, J.Rech.C.N.R.S., 34, 81 (1956).
323. F. HARARY, SIAM Review, 4, 202 (1962).
324. H. SACHS, Publ.Math.Debrecen, (a) 9, 270 (1962); (b) 11, 199 (1963).

325. L. SPIALTAR, J.Chem.Documentation, 4, 261 and 269 (1964).
326. H. HOSOYA, Theoret. Chimica Acta (Berlin) 25, 215 (1972).
327. A. MOWSHOWITZ, J.Combinatorial Theory, 12B, 177 (1971).
328. N. TRINAJSTIĆ, Croatica Chemica Acta, 49, 593 (1977).
329. A.J. SCHWENK, Ph.D. Thesis, University of Michigan, United States of America, 1973.
330. A. GRAOVAC, I. GUTMAN, N. TRINAJSTIĆ and T. ZIVKOVIĆ, Theoret. Chimica Acta, 26, 67 (1972).
331. M.J. RIGBY and R.B. MALLION, J.Combinatorial Theory B, 1979, in press.
332. L. COLLATZ and U. SINOGOWITZ, Abhandl.Math.Sem.Univ.Hamburg, 21, 63 (1957).
333. D. CVETKOVIĆ, Publications de la Faculté d'Électrotechnique de l'Université à Belgrade. (Série: Mathématiques et Physiques), No. 354-356 (1971).
334. T. ZIVKOVIĆ, N. TRINAJSTIĆ and M. RANDIĆ, Molec.Phys., 30, 517 (1975).
335. M.J. RIGBY, R.B. MALLION and D.A. WALLER, Chem.Phys.Letters, 59, 316 (1978).
336. S.F.A. KETTLE and V. TOMLINSON, Theoret.Chimica Acta.(Berlin), 14, 175 (1969).
337. G. KIRCHHOFF, Annal.Physik Chemie, 72, 497 (1847); (An English translation, by J.B.O'Toole, appeared in I.R.E. Transactions on Circuit Theory, CT5, 4 (1958)).
338. W. TUTTE, Proc.Cambridge Philos.Soc., 44, 463 (1948).
339. P.R. BRYANT, "Graph Theory Applied to Electrical Networks", in "Graph Theory and Theoretical Physics" (Editor: F. Harary), Academic Press, New York, United States of America, 1967, pp. 111-138.
340. W.-K. CHEN, "Applied Graph Theory", North Holland Publ.Co., Amsterdam, The Netherlands, 1971, Chapters 2 and 4.
341. R.B. MALLION, (a) J.Chem.Soc.Perkin Trans.II, 1973, p.235; (b) Biochemie, 56, 187 (1974).
342. E. CLAR, "Polycyclic Hydrocarbons", Vols. I and II, Academic Press, London, United Kingdom, 1964.
343. C.A. COULSON and G.S. RUSHBROOKE, Proc.Royal Soc. (Edinburgh), A62, 350 (1948).
344. M. GORDON and W.H.T. DAVIDSON, J.Chem.Phys., 20, 428 (1952).

345. T.F. YEN, Theoret.Chimica Acta (Berlin), 20, 399 (1971).
346. W.C. HERNDON, Tetrahedron 29, 3 (1972).
347. E. CLAR, personal communication to the author, December 31st, 1970.
348. R.H. MITCHELL and F. SONDHEIMER, Tetrahedron, 26, 2149 (1970).
349. M.J.S. DEWAR and H.C. LONGUET-HIGGINS, Proc.Royal Soc. (London), A214, 482 (1952).
350. R.G.A.R. MACLAGAN, Molec.Phys., 22, 821 (1971).
351. E. CLAR, personal communication to the author, April 22nd, 1971.
352. E. CLAR, "The Aromatic Sextet", Wiley, London, United Kingdom, 1972.
353. J.A.N.F. GOMES and R.B. MALLION, to appear.
354. C.A. COULSON and A. GOLEBIEWSKI, (a) Proc.Phys.Soc., 78, 1310 (1961); (b) Molec.Phys., 5, 71 (1962).
355. H. KUHN, Tetrahedron (Supplement 2), 19, 437 (1963).
356. C.A. COULSON and F. WILLE, Tetrahedron, 22, 3549 (1966).
357. J. GAYOSO, Thèse, Docteur Ès Sciences, Université de Paris, 1973.
358. (a) M. GOEPPERT-MAYER and A.L. SKLAR, J.Chem.Phys., 6, 645 (1938); (b) R.G. PARR, "The Quantum Theory of Molecular Electronic-Structure", W.A. Benjamin, New York, United States of America, 1964.
359. K. NISHIMOTO and N. MATAGA, Z.Phys.Chem. (Frankfurt), 12, 335 (1957).
360. H.W. VOS, W. BAKKER, C. MACLEAN and N.H.VELTHORST, Chem.Phys. Letters, 25, 80 (1974).
361. B.M. TROST and P.L. KINSON, J.Amer.Chem.Soc., 97, 2438 (1975).
362. R.B. MALLION, (a) Bull.Soc.Chim.France, 1974, p.2799; (b) Chem.Phys.Letters, 36, 170 (1975).
363. (a) H. HELLMANN, "Einführung in die Quantenchemie", F. Deuticke, Vienna, Austria, 1937, p.285; (b) R.P. FEYNMAN, Phys.Rev., 56, 340 (1939).
364. C.A. COULSON, Molec.Phys., 20, 687 (1971).
365. J.C. SLATER, J.Chem.Phys., 57, 2389 (1972).
366. S.T. EPSTEIN, (a) J.Chem.Phys., 60, 147, 3328 and 3351 (1974); (b) "The Variation Method in Quantum Chemistry", Academic Press, New York, United States of America, 1974.

367. A.C. HURLEY, Proc. Royal Soc. (London), A226, 179 (1954).
368. G.G. HALL, Philos. Mag., 6, 249 (1961).
369. A. TACHIBANA, K. YAMASHITA, T. YAMABE, and K. FUKUI, Chem. Phys. Letters, 59, 255 (1978).
370. J.A. POPLER Proc. Royal Soc. (London), A239, 550 (1957).
371. A. PINES, M.G. GIBBY and J.S. WAUGH, Chem. Phys. Letters, 15, 373 (1972).
372. H.M. McCONNEL, J. Chem. Phys., 27, 226 (1957).
373. R.B. MALLION, personal communication to Professor D.M. GRANT, February 12th, 1976; (Passed to Professor M. BARFIELD).
374. M. BARFIELD, personal communication to R.B.M., March 15th, 1976.
375. G.A. DIRAC, Proc. London Math. Soc. (Series 3), 2, 69 (1952).
376. O. ORE, Amer. Math. Monthly, 67, 55 (1960).
377. L. POSA, Magyar Tud. Alad. Mat. Kutato Int. Kozl., 7, 225 (1962) [cited in ref. 305].
378. V. CHVÁTAL, (a) "New Directions in Hamiltonian Graph-Theory", in "New Directions in Theory of Graphs". (Editor: F. HARARY), Academic Press, New York, United States of America, 1973; (b) Discrete Maths., 5, 215 (1973).
379. S. GOODMAN and S. HEDETNIEMI, J. Combinatorial Theory B, 16, 175 (1974).
380. E.F. SCHMEICHEL and S.L. HAKIMI, J. Combinatorial Theory B, 17, 22 (1974).
381. F.R. GANTMACHER, "The Theory of Matrices", Vols. I and II, Chelsea Publishing Co., New York, United States of America, 1960.
382. H.W. VOS, C. MacLEAN and N.H. VELTHORST, Molec. Phys., 35, 329 (1978)
383. A. AGARWAL, J.A. BARNES, J.L. FLETCHER, M.J. McGLINCHEY and B.G. SAYER, Canadian J. Chem., 55, 2575 (1977).
384. H. KELLER, E. LANGER and H. LEHNER, Monatshefte für Chemie, 108, 1371 (1977).
385. R.J. ABRAHAM, S.C.M. FELL and K.M. SMITH, Organic Magn. Resonance, 9, 367 (1977).
386. R.J. ABRAHAM, in "Proceedings of the 11th Jerusalem Symposium on Quantum Chemistry and Biochemistry" (Editor: B. Pullman) Reidel, Dordrecht, The Netherlands, 1978, p. 461.
387. K. MÜLLEN, (a) Helv. Chimica Acta, 61, 2307 (1978); (b) Personal communication to RBM, April 21st, 1976 and January 13th, 1977.
388. R.C. HADDON, M.L. KAPLAN and J.H. MARSHALL, J. Amer. Chem. Soc., 100, 1235 (1978).

"And from my neck so free
The Albatross fell off....."

[From the Rhyme of the Ancient Mariner
(Part IV)]

.

"He went like one that hath been stunn'd,
And is of sense forlorn:
A sadder and a wiser man
He rose the morrow morn."

[ibid., (Part VII)]

S.T. COLERIDGE
(1772-1834)