INTERACTIVE COMPUTER GRAPHICS
IN QUANTUM CHEMISTRY RESEARCH

by

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ABSTRACT

The broad aim of this thesis is to investigate the feasibility of using interactive computer graphical methods to control experiments in scientific research. A particular area of scientific research, namely quantum chemistry, is chosen because within it the widely used semi-empirical methods provide an excellent framework, from both theoretical and practical points of view, upon which to base the investigation.

The first chapter discusses interactive computer graphics in general terms, and reviews the origin, development and a few significant applications of graphical techniques, before briefly considering some aspects of hardware, software and graphics systems design.

In the second chapter the specific advantages which graphical techniques offer in scientific work are examined against the background presented in chapter one. Then, after reviewing the nature of the chosen problem area and the conventional role of the computer, attention is turned to the question of designing a graphics system for use in quantum chemistry research.

The third chapter describes in detail an experimental yet comprehensive system developed for this purpose on an ICL 4130 computer equipped with a graphical display device. The design of the system is related to the typical problem-solving phases used in many areas of scientific work, but which are particularly well defined in the chosen area of quantum chemistry. The system also takes advantage of the many opportunities for graphical displays presented in each of the phases so defined. The form of control adopted is through a 'menu' type of dialogue, where at

each decision point in the course of an interactive session, a list of available options is displayed to the user. Selection is then made by light pen, console key or typewriter keyboard.

The fourth and fifth chapters describe practical experiments with the graphics system, dealing with properties of SCF ground states and excited states respectively.

The sixth and seventh chapters contain theoretical studies of phosphonitrilic polymers which emerged partly from a consideration of extending the range of applications to molecular systems beyond the 'standard' molecules with well-known properties which are used for designing and illustrating the graphics system in the earlier chapters. The concept of the 'island' orbital in such molecular systems is discussed in detail at both the Huckel and SCF-CI levels of approximation, and the analysis finally leads to conclusions regarding the influence of island orbital solutions on the UV spectrum.

PREFACE

The interactive graphics system described in detail in this thesis has been designed as part of the research project and has been successfully applied to some illustrative problems within the π-electron approximation. It had been hoped at the outset that time would permit extensions of the system to include some of the more recent ZDO-SCF all-valence-electron methods. Similarly it was hoped that further comparative analyses of the various SCF parameter schemes already built into the system could be carried out.

However, as with all large scale computing projects, the inevitable difficulties arose, causing frustrating delays in the development of the graphics program. This, being one of the first major projects with the graphics installation at Keele, stretched the facility to its limits at the time. These limits and some unfortunate machine and associated system faults were, in many cases, only recognised for the first time when encountered by this project. The worst faults took the form of randomly active 'bugs', which caused mysterious run-time errors and consequent abandonment of the graphics program in mid-session. Only rarely would the fault manifest itself at the same point in an immediately re-run program, and, thankfully, several sessions would be totally free of such problems. Apparently the same type of fault has been observed with similar graphics installations elsewhere, and some 4100 Fortran compiler problems are currently under investigation by the 4100 user's group.

Nevertheless, the quantum chemistry interactive graphics system as it now stands incorporates many desirable features and it is already capable of providing useful results more quickly and more effectively than conventional computing methods. Furthermore, it is sufficiently flexible in its basic design to accommodate modifications and extensions along the lines suggested above as soon as the physical difficulties mentioned can be overcome.

CONTENTS

INTRODUCTION

A prime objective of this work is to examine, analyse and solve in some way the problems associated with the use of an interactive graphical display device linked to a computer to control and conduct experiments in scientific research.

The particular field of quantum chemistry chosen to form the scientific or theoretical framework of study for this purpose is especially appropriate since it provides examples of many different aspects of the problem. These may be summarised as follows -

(1) A model described in terms of adjustable parameters - the properties of the model can be studied in relation to variation of the parameters, with the results expressed in graphical form.

(2) Solutions of an approximate Schrodinger equation, which in a sense characterise solutions of this equation, and may therefore be used to illustrate graphically and thereby help consolidate the understanding of concepts that are described theoretically.

(3) Quantities derived from the solutions which are used for interpreting and describing experimental observations. Typical quantities are associated with the ideas of thermo-chemical stability, chemical reactions, various forms of spectroscopy and so on. Comparisons between computed quantities and experiment over a wide range of phenomena may be studied effectively with the aid of computer graphical techniques.

(4) Interesting theoretical relationships within the model itself, which can be studied both analytically and numerically, and illustrated effectively by display techniques.

In addition, the experimental procedure which employs the type of model considered here is well structured, not merely in relation to computational methods, but also for projection into the interactive graphics setting. It would seem to be one of the most satisfactory fields of study for this purpose since it embodies such a wide variety of typical operations and functions, which are often encountered in other systems of study, but possibly with less frequency and scope.

The work described in this thesis is, therefore, a study of a selected part of quantum chemistry research in terms of objectives defined in relation to the implementation of interactive computer graphics as an extension of the conventional use of the computer in this field. It is not intended to engage in quantum chemistry research as such, although a substantial later part of the thesis is in fact devoted to theoretical studies of phosphonitrilic polymers which arose during the course of the work. Otherwise the graphics applications presented are based on problems which are fairly well understood, and which therefore provide established properties and relationships which can be used for design and test purposes.

Hence the central part of the thesis is concerned with the definition, organisation and design of an interactive graphics system in relation to the nature of the scientific problem to be solved and to graphics techniques, using known results to demonstrate the range of facilities offered by such a system.

CHAPTER ONE

INTERACTIVE COMPUTER GRAPHICS

This first chapter contains a survey of the broader issues concerning the general application of interactive graphical computing methods. The aim is to define the context in which an interactive graphics system for use in scientific research may be designed and implemented.

A brief introductory section discusses the origins and the growth of graphical techniques in general, and interactive computer graphics in particular. This is followed by an account of some recent applications in a variety of areas, from which common advantages and difficulties in applying graphical methods are seen to emerge.

Hardware and software provision for interactive graphics is discussed in a separate section, and is related in the final section of the chapter to some general principles of design for interactive computer graphics systems.

1.1 The Origins of Interactive Computer Graphics

The value of the graphical representation of empirical quantities arising in science and engineering has been realised for many years. Graphical methods have traditionally been used to assist in establishing laws and analytical relationships between variables, and to convey quantitative information in a manner which is both concise and easily understood.

More recently, graphical techniques have found application in a wide range of additional areas, including the display and analysis of statistical data, and the construction and analysis of symbolic models, such as flow charting, simulation and scheduling diagrams. The techniques are also well established in the field of design applications, notably in architecture, electronics and heavy industry.

Many of the graphical techniques used in the areas mentioned have, of course, grown up independently of the computer, but in each case the computer is now sometimes used to produce output in graphical form. In fact, the development of graphical computer output facilities has proceeded much more slowly than has the growth of other computer facilities, and only relatively recently in computing history has attention been paid to the question of programming the machine to perform the calculations and to produce graphical output of the results, all in a single computer run. Graph plotters may sometimes be satisfactorily used for this purpose but they operate extremely slowly in comparison with general computer processing. This is of no great consequence if the plot is known in advance to be what is required, since the graphical information may be stored, in code form within the computer, and the actual plotting operation can be undertaken later, at some convenient time. However, when a sequence of further computations depends upon an analysis of the plot, the delay is likely to be considered more significant. More appropriate for operations of this type are display devices based on a cathode ray tube, which are capable of producing graphical displays almost instantaneously.

The availability of such devices has enabled graphical techniques to be used in interactive computing, with three particular advantages for applications in those areas where graphics already had an important part to play.

(i) The scope for creative development by the user is widened through being able to identify, move, modify and replace selected parts of the displayed image - as is possible when the display device in use is equipped with a light pen or similar mechanism.

(ii) Analytical processes are enhanced through the provision of immediate visual access to the results of curve and surface fitting operations etc.

(iii) Overall control of the processing sequence can be achieved through commands issued via the display device; decisions on the course to be taken by the program are based on an evaluation by the user of the displayed information.

Perhaps the earliest example of interactive computer graphics was the SAGE system, developed by the US Department of Defence in the 1950's, {1}. SAGE presented visual information on aircraft positions, and permitted requests for more detailed information to be made by pointing a light pen at targets on the display. It was the fore-runner of several military graphics-based information systems, {2}, and also laid the foundations for further advances in graphical hardware and software.

In the early 1960's the 'sketchpad' project was developed by Sutherland, {3}. This is often claimed to be the first interactive computer graphics system specifically aimed at computer aided design. Much of the hardware used had origins in the SAGE project.

At about the same time as Sutherland's research work was being undertaken at MIT, developments were also taking place in the commercial sector, with Itek laboratories producing a system for lens design. Both systems had several features in common. Each permitted retrieval of coded pictures from backing store or from core, and each included facilities for retaining information about the topological relationships of picture elements. In addition, both systems had provision for producing hard copy output of displayed material. These systems also advanced the development of other concepts often associated with computer graphics, namely file handling and data structure techniques.

Another early major research programme was conducted by General Motors who, in about 1959, began work on DAC-1, a computer-aided design system for the automobile industry. This project was notable for the contribution made by IBM to the design of special graphics display consoles, which were to become prototypes for the IBM 2250 unit, currently used in many graphics systems.

These early projects laid the foundations for what has come to be known as interactive computer graphics, establishing many of the basic principles and techniques which remain in use today. In the last ten to fifteen years many technological developments have taken place, and the range of applications has increased considerably.

Three areas of application and some of the more recent projects within them, which have implications for the major topic of this thesis, will be examined briefly in the following section.

1.2 Applications of Interactive Computer Graphics

For a long time, high equipment and development costs have limited applications of interactive computer graphics to two main general areas. These are

(i) command and control, where typical applications include air traffic control and management information systems, and

(ii) computer aided design, where the major applications have taken place in the motor, aircraft and ship-building industries.

Hantman, {4}, has distinguished the main characteristics of systems in these two areas. Design oriented systems place the emphasis on drawing and manipulating graphical information, using the computer to assist the designer in simulating and viewing the results of a creative process. On the other hand, command and control systems require less creative ability on the part of the user, but require a greater ability to pick out quickly the relevant information from the display, and to undertake actions which have the effect of changing system parameters, or of modifying the stored information.

1.2.1 Command and Control Systems

Many command and control systems are based on the interactive use of a type of cathode ray tube display device (VDU) but, since the information presented by these displays is in purely alphanumeric form, they cannot be classified as interactive graphics systems. Amongst these are the real-time systems designed for dealing with hotel and airline seat reservations etc.

Henderson,{5}, describes a company's transition from cards and paper, through alphanumeric displays, to fully interactive graphics, as the basis for a management information system. Each of the company's functional areas - marketing, engineering, manufacturing, finance, accounting and administration had foreseen advantages which the graphical presentation of information might offer, but cost considerations had up to the time of writing, prevented a complete changeover to graphics from taking place. Nevertheless, greater profitability and a better service had already materialised where the implementation of computer graphics had been possible.

The cost factor undoubtedly prevents the more widespread use of graphics in this general area. Military applications, however, appear to be increasing in number, {2}.

1.2.2 Design Oriented Systems

Great strides have been made recently in the use of interactive graphics for computer aided design. In several instances, large industrial firms have collaborated with computer manufacturers to produce successful systems. Applications have taken place in such fields as

Civil engineering - bridge, road and building design,
Motor, ship and aircraft design,
Engineering - drawings, machine tool control, electronic circuit design,
Chemical plant and pipeline design,
Textiles,
Optics.

Detailed descriptions of many such applications are given by Green and Parslow, {6,7}, and by Faiman and Nivergelt, {8}. Several accounts of design work in the aircraft industry also appear in Prince, {9}.

Partington, {10}, describes the direct approach taken to interactive graphics in the Ford Motor Company. All considerations not directly related to the use of the display device and the light pen were excluded. The goal was to develop an easily used graphics facility for the company's technical community, and the approach taken led to a productive operational system in just over two years. A small computer attached to a graphics display unit was used as a 'stand-alone' system, in the first instance, and all necessary graphics applications programs - for drawing lines, tracking the light pen etc - were written in FORTRAN. Claimed advantages for this type of arrangement were

(i) flexibility and cost savings when expanding the system - increase the number of small installations,
(ii) no interface with fully occupied batch processing machines,
(iii) greater reliability through operating independent units,
(iv) no propagation of programming errors between units,
(v) better response times,
(vi) mobility of small units improved the acceptance of graphics by new users.

Selected jobs were programmed jointly by system programmers and application specialists, training programs were arranged, and the system was then put into general use. Early success quickly justified a second similar system in another department. Through careful programming, large-scale problems have been solved quickly and relatively cheaply without the need for large-machine support.

Interactive graphics is now firmly established in the general area of computer aided design, and, as more relatively cheap display devices are developed, the range of applications can be expected to increase.

1.2.3 A System for the Real Time Solution of Technical Problems

Sewell, {11}, describes a project in an area different from the two areas discussed so far, but closer in many ways to the project to be described later in this work.

The project investigated the suitability of graphical techniques as an aid to solving fractionation problems. Fractionation is a widely used petro-chemical process by which the components of feed mixtures are separated into product streams with specified purity requirements.

In contrast with the Ford project of section 1.2.2, here it was necessary to ally graphics capabilities to large existing programs, and to retain the power of a large computer. The standard algorithms in use involved the manipulation of many variables. Hence it was thought that interactive graphics would be the ideal mode for controlling the operations quickly and effectively, and for analysing intermediate and final results. Since the calculations were performed frequently, savings in overall computer time were expected, in addition to the expected savings in capital costs through improved solutions of the problem. The system was designed to -

(i) be flexible - giving the user full freedom to obtain an optimal solution,

(ii) provide the user with the opportunity to improve on batch type solutions,

(iii) give fast response time,

(iv) shorten run time, through interactive elimination of unnecessary calculations,

(v) fully utilise the graphical display for concise presentation of analytical and control information.

Interaction was achieved through the alphanumeric keyboard and a light pen attached to the display console. Each display consisted of areas reserved for titles, messages, data and graphical material, and control texts, respectively. Lists of optional procedures, from which a selection by light pen could be made, appeared in the data area at appropriate decision points in the program, and standard control commands, such as 'PROCEED', 'RESTART', etc, were given in the control text area.

Early experience, as reported by Sewell, suggested that the system was fulfilling the design aims. In particular, the user found he could eliminate the time previously spent searching through tables and manuals, and was therefore free to concentrate his efforts on solving the given fractionation problem.

1.3 Advantages and Disadvantages Associated with the Use of Interactive Computer Graphics

Some of the commonly encountered advantages and difficulties connected with the design and operation of interactive graphics systems have already been noted in the applications descriptions given in the previous section. These are largely typical of the more general benefits and problems which will now be summarised.

1.3.1 Advantages

The main advantages over conventional computing methods which interactive graphics systems can offer come under the two broad headings

(a) Saving of project time,

(b) Improved solutions

Both of these can, as in the case of the project described in 1.2.3, also result in related cost savings.

Discussing an application in the aircraft industry, Boyles, {12}, claims the time taken to complete a preliminary design process was reduced to one tenth of the 'pre-graphics' duration. Similar substantial reductions are claimed by Levick, {13}, in another aircraft design process.

The time, and hence cost, savings attributable to interactive computer graphics generally arise out of various combinations of

(i) Faster input/output - enables decisions to be made and acted upon more quickly,

(ii) Input and output may be selective,

(iii) Only relevant sections of programs are entered,

(iv) Only relevant data are stored, and may be quickly retrieved,

(v) Speedier extrapolation to optimal solutions is achieved through graphical presentation and analysis of intermediate solutions,

(vi) Previously computed solutions may be stored and quickly retrieved to guide the user in his efforts to find a solution to the current problem,

(vii) Results are more easily conveyed between sections and to management.

In addition to saving both time and money, several of the factors listed above also contribute to an improvement in the quality of solutions. Cornish, {14}, stresses the need to maintain, and where possible to improve the quality of solutions beyond what was previously obtained using conventional computing methods. However, the facilities afforded by a graphics display unit for rapid, creative and decisive interaction with the computer have undoubtedly led to superior results from a large number of applications in the areas of design and control.

Certain other advantages which interactive computer graphics has to offer when applied in research work will be discussed in the following chapter.

1.3.2 Disadvantages

The four main difficulties limiting the growth of interactive graphics are

(i) cost

(ii) acceptability

(iii) implementation problems

(iv) software problems

The initial cost of involvement with graphical systems is inevitably high. Although new, lower-cost hardware is becoming available, and software support from manufacturers and commercial organisations is improving, a graphics system still represents a substantial capital outlay. Other items contributing to initial costs include staff development, conversion of existing programs, and trial runs with the new system. Some time may elapse before the savings indicated in 1.3.1 begin to materialise.

The acceptability of an interactive system depends on its efficiency and the ease with which it can be used. The man-machine dialogue must be conducted at a level and at a pace which is acceptable to all potential users of the system. Unfortunately multi-purpose dialogues are difficult to write, and require large quantities of computer storage. As a result, conversations tend to be at a single fixed level, which can be difficult for the new user, and frustrating for the experienced user.

Response times, particularly when the graphics system is time-shared, can also prove to be an important factor contributing to overall acceptability.

Implementation difficulties can arise in several ways. The main problems are likely to occur when attempts are made to modify existing batch type programs to work with the graphics system. It may be necessary to make these more compact, so as to accommodate graphics software, or to make them more efficient in order to keep response times down, or to otherwise make modifications, any of which may accidentally corrupt established routines.

Behavioural problems can also affect the success of an implementation. Apart from the well known human resistance to change, genuine dissatisfaction with the system may be causing the difficulty. The system should be designed with the co-operation of all the users, and pilot runs in the development stage should be used to test user reactions.

Software for graphics programs will be considered in some detail in the next section. However, software remains as a problem area for graphics, despite the availability of general purpose packages of subroutines, such as the IBM GSP, {15}. As yet there is no universally applicable high level language for graphics applications, so the writing of programs for graphics is a skilled and time-consuming task.

1.4 Hardware and Software for Interactive Computer Graphics

This section summarises and describes the purpose of equipment currently in general use for interactive graphics, and discusses the provision and use of software for graphics systems.

1.4.1 Hardware

An interactive computer graphics terminal is usually structured as a peripheral to a large computer. The basic units which constitute a terminal are

Display data channel
Display controller
Display console
Input devices such as keyboard, function keys, light pen etc.

The light pen and similar devices permit the user to indicate an element displayed on the screen, for control or analysis purposes. Recent developments, {16}, include a mechanism which allows displayed items to be indicated by moving a stylus on a horizontal tablet placed in front of the screen.

The function of the basic hardware is to allow an application program in the central processor to use the display for graphical output. By using the input devices, the user can control the flow of this application program, and can input data to it. Graphical commands, output from the program, are stored in core as a display file. The set of commands, which describes the picture to be drawn, is accessed regularly by the display data channel and sent to the display controller. On receiving each command, the controller activates the appropriate function generating hardware, and this in turn controls the position of an electron beam, which produces the illuminated picture on the screen. Every command must be individually processed to complete the picture. The entire sequence is repeated or 'refreshed' about fifty times a second to give a continuous image on the screen.

There are three main types of interactive graphics installation in common use

(a) Dedicated stand-alone systems

(b) General purpose display systems

(c) Time shared systems

The first type comprises a processor, display input and output equipment, and associated peripheral equipment used for one or more specific graphics applications programs. These systems, usually highly priced, often combine specialised hardware and software, and are found most often in large organisations or research establishments.

The second type of installation uses a processor normally available for non-graphics applications, but capable of supporting various graphics applications when required - thereby spreading the cost of the graphics facility. There are many graphics devices which may be linked to the large computer. These range from simple display terminals to sophisticated satellite computer systems.

For example, the IBM 2250 (model I), consists of a viewing unit with interaction devices, a display processor and a display file held in a separate 8K byte core store. The screen can be refreshed without recourse to the supporting computer, but all attentions, e.g. light pen detects, interrupt the central processor for servicing.

The Elliott 4280 graphics unit is similar in its operation, but the display controller has autonomous access to the core of a 4100 computer in which the display file is held. This method allows a more flexible allocation of core, but imposes restrictions on the allowed distance between the display console and the main computer.

There has been a recent trend towards satellite graphics systems, consisting of a small dedicated computer interposed between the main computer and the display processor. The advantages given by this arrangement are

(i) provision of limited 'stand alone' facility, independent of the 'host' computer,
(ii) full facilities of main processor available for large calculations and administration of the data base,
(iii) flexibility for positioning of equipment,
(iv) possible use of multiple display consoles.

The third general type of graphics installation provides graphics terminals as part of a general time-sharing system, an approach which can reduce the overall cost of the graphics facility and permit relatively cheap expansion. This is offset by the need to provide a larger central processor and a more sophisticated operating system. The major drawback is the relatively slow response which can be obtained as the graphics user competes with other interactive users.

1.4.2 Software

In any type of graphics system, three levels of linked software can be identified

(i) The operating system,
(ii) Applications programs,
(iii) Graphics software.

The operating system, under the direction of the user, activates the applications program which, in turn, calls routines, as specified, from the graphics systems software. Storage for data, normally implying a structured data base, a display file and a correlation map must also be provided. These are linked as shown in figure 1.1.

Few operating systems are 'graphics-oriented', and a user will generally expect to have to compete, often unfavourably, with other claims on the computer's versatility.

Applications programs are often adapted versions, written in a high level language, of existing batch type programs.

Of the high level languages in common use, ALGOL and FORTRAN possess particular deficiencies when considered for graphics applications. ALGOL is weak on data manipulation, whereas FORTRAN is a little better in this respect, but possesses some obscure, dated input-output features. PL/1 offers more comprehensive data handling and better input-output facilities than both ALGOL and FORTRAN. However, each of these three languages has the disadvantage of not being specifically designed for conversational use.

Yet conversational languages such as JOSS, {17}, BASIC {18}

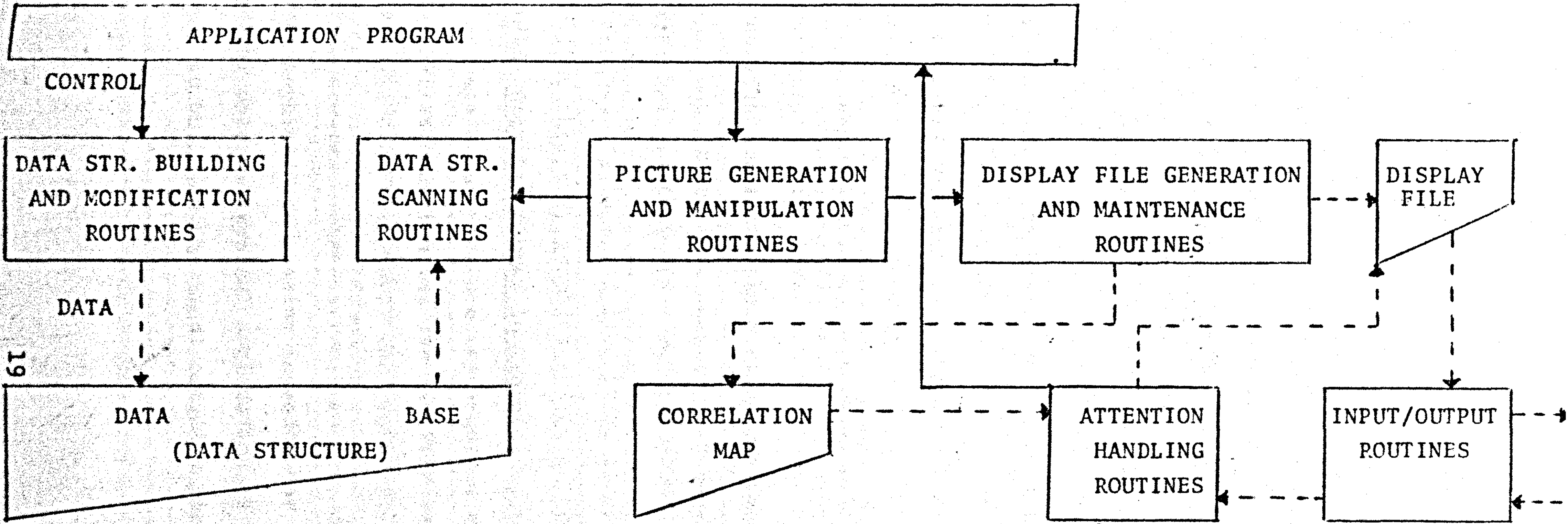
APPLICATION PROGRAM
CONTROL
DATA STR. BUILDING AND MODIFICATION ROUTINES
DATA STR. SCANNING ROUTINES
PICTURE GENERATION AND MANIPULATION ROUTINES
DISPLAY FILE GENERATION AND MAINTENANCE ROUTINES
DISPLAY FILE
DATA
DATA BASE (DATA STRUCTURE)
CORRELATION MAP
ATTENTION HANDLING ROUTINES
INPUT/OUTPUT ROUTINES

Fig. 1.1

and QUIKTRAN, {19}, are because of limited program and data structure facilities, more suited to simpler problems than to large interactive applications.

Graphics software has been incorporated in extended versions of both ALGOL and FORTRAN, named as AED, {20} and GRAF, {21}, respectively, but neither of these can be regarded as being a general purpose graphics language. A recent attempt to produce such a language is METAVISU, {22}, which has been applied to a range of problems, including circuit design, architectural drafting and statistical data analysis. But, even at the time of unveiling of this language, the general view was expressed that an easy-to-use, machine and problem independent, high level graphics language was still a long way off, {23}.

A compromise is to link applications programs written in a conventional high level language with a graphics software package, consisting of subroutines which may be called to deal with display code generation, display file management, attention handling, light pen tracking etc. The ICL FRED package, {24}, is of this type, and it, in a modified form, is used extensively in the quantum chemistry graphics system to be described later.

1.4.3 Data Structures in Graphics

Data structures are important in graphics for two reasons.

First, substantial use is often made of various kinds of tree and ring structures and linked lists when a display file is being created. These structures are, however, not generally very sophisticated, being intended for use by the display processor only. A typical application is where subpictures are used to build up the final complete picture, the subpictures being single data blocks in the data structure which may be referenced as required for inclusion in the overall picture.

The second main use of data structures in graphics programs arises out of the need to build and manipulate a problem-oriented data base. Graphics applications often require to create small sets of items, gathered together from a large data set, for display and analysis. It is important that these items and their associated attributes are stored in such a way that the selection operation for a display is made as efficient as possible.

Except in special situations where a dual-purpose graphical data structure is used, the display file organisation and the problem-oriented data base are regarded as largely separate considerations.

1.5 Systems Design for Interactive Computer Graphics

Graphics system design is the operation of bringing together, with due regard to physical, time and cost limitations, the correct hardware and software components, so that they work efficiently in the application for which the system is intended.

The components and constraints, some of which have already been briefly examined, must be carefully considered alongside the overall aims of the graphics system.

1.5.1 Types of System

Newman and Sproull, [16], have identified three different types of interactive graphics system, each designed to meet the needs of a different class of user. They are

(i) Picture-editing systems,

(ii) Specialised application systems,

(iii) General-purpose graphics systems.

Picture-editing systems are those where the graphics display is used simply as a powerful drawing board. Symbols and sub-pictures may be created on-line and used to form pictures and diagrams. A command language permits the input of instructions, usually typed function names, which cause modifications to be made to the display file, and hence to the display. A distinguishing feature of this type of system is that quantitative analysis of the displayed material is not usually allowed for in the design.

The specialised application systems are specifically designed for a single purpose such as circuit design or data analysis. In many of these applications the bulk of the programming is non-graphical, the display serving as a fast input-output device.

The general-purpose system is one that provides, for the applications programmer, graphics facilities, a high level language, complete with aids for de-bugging and editing, and powerful data structure facilities. With this type of system, the programmer is better able to concentrate on the less routine aspects of his task, and should find the writing of a graphical program no more difficult than the writing of a conventional one.

1.5.2 Hardware and Software

Having identified the aim of a specific graphics project, and the broad design category in which the system is to be developed, attention can be turned to hardware and software requirements.

Some of the relative merits of stand-alone, host-satellite and time sharing systems have already been discussed. The type of hardware best suited to a particular application must be decided from such considerations as capital and running costs, response time requirements and flexibility. Estimates must be made of the likely storage and computational requirements in order to give an indication of the type and size of facility most appropriate to the application. Skyrme, {25}, has proposed a scheme for classifying applications by the frequency of attentions and the order of magnitude of the calculations performed between attentions. He also goes on to give recommendations for the type of installation most appropriate for each application class.

Applications and graphics software are likely to depend to a large extent on the choice of hardware, or on historical factors if the project is to use converted existing batch type programs. Within the range of freedom available, however, useful consideration can be given to both applications program and dialogue design.

1.5.2(a) Applications program design

The applications program is best written as a tree structure of options. The whole suite of routines may well be too large to fit into core at run time. One way round this problem is to reserve an area of core for each level in the tree, just large enough to accept the longest routine in that level. Routines of the same level can then be over-layed when called, parallel routines being unable to interact with each other. A running program can thus consist of one routine from each level, all in core simultaneously.

Such an arrangement also makes for easier adaptations and additions to the program, as well as assisting interactive control of the program.

1.5.2(b) Choice of dialogue

The main considerations to be born in mind when deciding on the mode of interactive dialogue are - the purpose of the dialogue, its suitability for the particular application, and the user, who in many instances will be a different person from the programmer.

The aim of the dialogue is to offer concise understandable information to the user at certain points in the running of the program. This may be used as a basis for seeking further information, or for deciding how the program should proceed from that point. There are several ways of achieving this, two of which have been used most widely.

The first type of dialogue is essentially user initiated, commencing with the user typing in a command selected from a limited vocabulary. This command could be to initiate a computational procedure, the storage or retrieval of a data item, or a branch to another section of the program.

The second type of dialogue is machine initiated, since the display containing a menu of available options appears automatically at each decision point in the program. Selection is usually made by light pen or by display console keys which relate to the menu items, the action initiating one of the processing operations as above.

The typed command is more suitable when a full alphanumeric keyboard is attached to the display console, and has a particular advantage in that the dialogue can be designed so that abbreviated commands are accepted. This is very convenient and saves time when the user has become more familiar with the command vocabulary. On the other hand, the menu approach permits more complete textual information to be presented, and the menu items are easily modified or deleted.

Several programs combine the best features of each of the above basic forms of dialogue, reserving a general display area for graphical information and menu items, and a smaller separate area for control commands.

1.5.3 Program Control

The well designed graphics system never leaves the user in doubt as to the current state of the program or as to what his alternative courses of action are. This means that decision points have to occur often enough in the running program, and with just the right amount of information, concisely displayed, to enable analysis and control decisions to be made in a reasonable length of time. The time allowed for such decision making will vary from one type of installation to another. Generally, more 'think' time is likely to be available with a time shared system than with other types of system.

A modular tree structure for the program, as indicated in 1.5.2(a) facilitates free and comfortable 'movement' between sections and helps to give a positional understanding of the system to the user.

User errors should be recoverable in a straightforward way, but to help avoid them it is advisable to include a procedure which must be followed by way of confirming a decision action. For example, when using a menu type of dialogue, the selected item may be made brighter, or all others may be deleted, before a further user action causes the command to be obeyed.

1.5.4 Testing the System

At the development stage it is useful if all potential users can participate in tests, in order that

(i) points of suspect clarity or redundancy in the dialogue or in display material can be identified and corrected,

(ii) all the likely 'routes' through the programming system can be evaluated for comfort in use

(iii) extended tests of system performance with realistic data can be undertaken,

(iv) response times of the system can be examined, and efforts can be made to reduce them if necessary - Martin, {26}, gives some suggested maximum response times for different types of operation.

Thus many closely related factors need to be taken into consideration when designing a graphics system. It is difficult to map out a universally applicable algorithm which will lead to an optimal design in a given situation. Instead, an attempt must be made to consider all the factors together, so as to produce a well-balanced system, capable of achieving the specified aims quickly and accurately.

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CHAPTER TWO

INTERACTIVE COMPUTER GRAPHICS IN SCIENTIFIC RESEARCH

In the first chapter some general principles and issues concerning the design and implementation of interactive computer graphics systems were discussed. In the present chapter attention is turned specifically towards the study of computer graphics within the field of scientific research, discussing both its advantages and the way in which the scientific problem conditions the design of a graphics system.

To illustrate the use of graphics in science, a specific field of research has been chosen as a basis of study, namely the area of semi-empirical methods within quantum chemistry. The quantum chemistry problem manifests many interesting features which are characteristically associated with scientific problems in general, and, furthermore, offers good and varied opportunities for utilising computer graphics. It, therefore, provides an ideal framework for study in both the research and development areas of computer graphics applied in science.

The first section of this chapter considers the use of computer graphics in scientific research, both as a technique and in relation to the way in which scientific problems are often broken down into sections or phases which follow successively in the formulation of a solution process. These ideas are then carried over to the quantum chemistry problem, where the breakdown or subdivision into solution phases is discussed more specifically in terms of a statement of the overall problem. The same subdivision is then related to both control and examination of procedures and results by interactive computer graphics. The final section of the chapter considers the practical issues which arise in the design of a graphics system for use in the selected area of study.

2.1 Graphics in Scientific Research

Non-computer based graphical techniques are well established in many branches of scientific research. Graphical methods play a part in all phases of application of the scientific method, but perhaps most significantly in the initial modelling of the system and later in the analysis of results obtained from the model.

Recent technological advances have enabled the computer to contribute automatically to graphical work, and many useful applications of computer graphics in various areas of scientific research have been made. These applications have, however, largely concentrated on those same phases of the work which are traditionally associated with non-computer based graphical techniques.

Computer graphics in modelling tends to be based on specially written software, though if in fact a model is described geometrically, some general purpose routines may be available for synthesising models, constructing segments, manipulating scenes by translations, rotations, expansions and contractions, and by offering projection and perspective facilities.

Graphics routines of this type, which have been used extensively in computer aided design, have proved extremely useful in the study of large molecules and crystal structures as described by Levinthal, {1}, and by Okaya, {2}, respectively. Barry and co-workers, {3}, have also described how stereoscopic displays of molecules have been produced and manipulated using a small computer. The facility to build up and manipulate models by computer graphics clarifies relationships and structures within the models, and enables this important phase of an investigation to be carried out more effectively than might otherwise be possible.

The second category of applications referred to above, relates to later stages of the research procedure and is concerned with the display and analysis of data. Standard packages are also sometimes used in this area of computer graphics and such packages typically include data-display routines, transformation and curve and surface fitting routines. General curve fitting packages related to graphical display methods have been produced by Knott and Reece, {4}, and Priver, {5}. Spline functions, rational cubic polynomials and Bezier polynomials, {6}, are all in current use as representations of curves. Many of the techniques used for describing surfaces are based on the work of Coons, {7}, and make use of the so-called Coons surfaces which are collections of 'patches' i.e. four sided curvilinear surface sections. Recent developments in techniques for curve and surface fitting have been reported by the computer-aided design group in Cambridge, {8}, where the range of graphics design applications has extended from glass bottles to ship's hulls. One commercially available package for graphical analysis of three-dimensional data is GATD, produced by IBM {9}. This package includes facilities for providing a wide variety of data displays, together with routines for data manipulation and surface fitting.

Computer graphics is undoubtedly capable of making substantial contributions to the data and results analysis stage in scientific research. Graphs and diagrams are relatively easily programmed for display on the screen, complete with axes, tables and other information. Scales and relative positions of elements in the display may be adjusted interactively to achieve greater clarity of presentation, and, when the image has been transformed to a satisfactory form, program segments can be invoked to produce a hard copy on a graph plotter. If required, a well-drawn, neatly arranged display can be filed, under program control, into permanent computer records for subsequent analysis, comparison purposes or as a guide to further experiments. In fact all the activities which are part of this final phase or stage of the research process can be effectively and substantially enhanced by the use of computer graphics.

Graphical techniques tend, in practice, to be restricted to either the early modelling phase or the final analysis phase of the process. Although the visual representation of a model has its own special value, the analysis to which the image points is rarely, if ever, conducted immediately, on-line and interactively with the display. Similarly, the operations of data analysis are usually regarded as activities completely separate from those by which the data set was created. The complete research process has seldom, if ever, been carried out through the medium of interactive graphics.

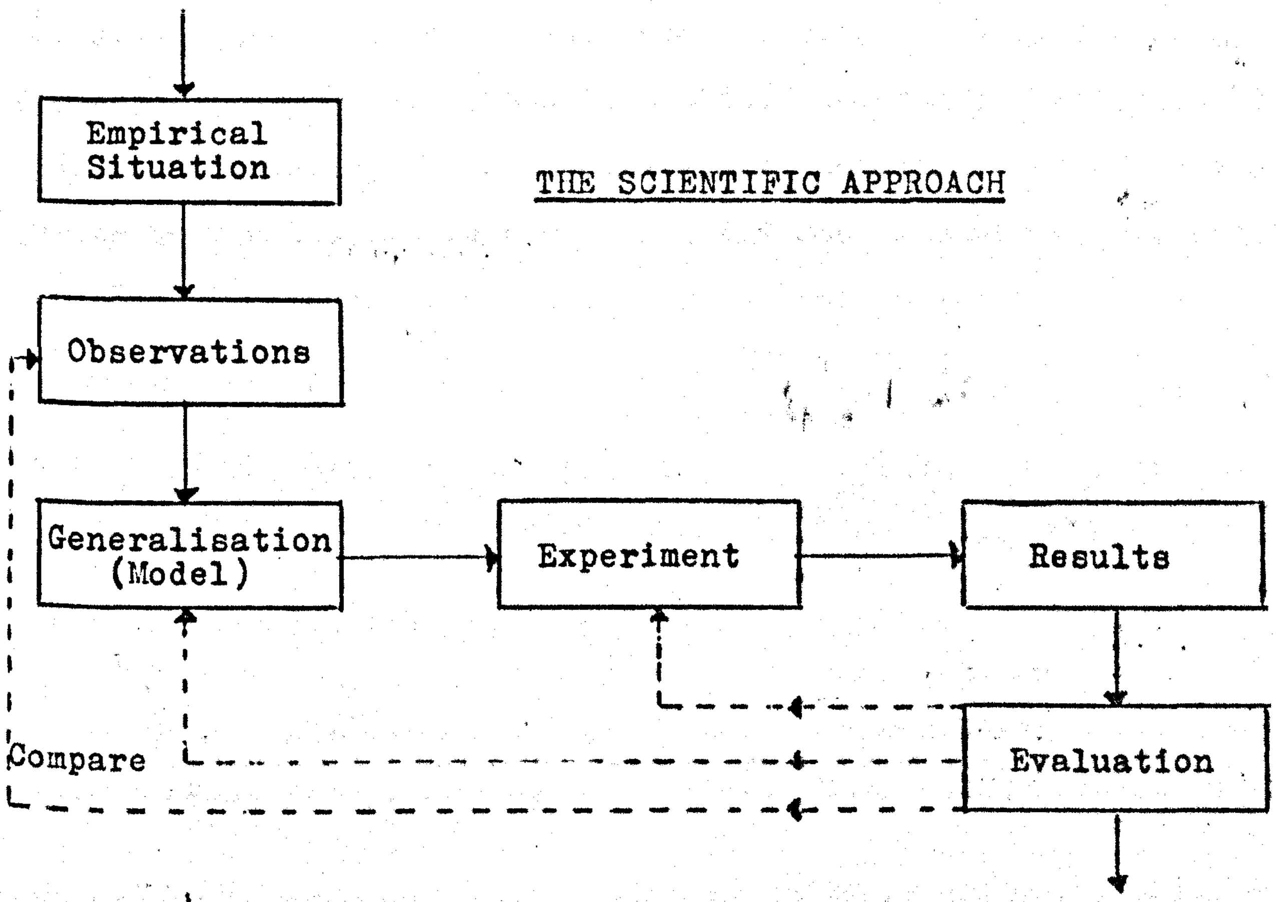
This is, however, the context in which the present work has been undertaken. Its main objective is to investigate how interactive graphics can be designed to bring together and control the various stages of definition and analysis which constitute the complete statement and solution of a scientific problem. It is not the intention to examine the use of computer graphics as applied solely to any one stage of the process, however demanding and interesting this may be. The interest here is essentially in studying a <u>complete</u> problem and its control and analysis by interactive computer graphics.

Before moving on to a more precise definition of the project, it is worth considering briefly a few more aspects of computer graphics in relation to the scientific problem solving process.

1. Substantial programming effort is required to produce the advanced dynamic displays used to manipulate and to visually analyse complex structures such as crystals, large molecules etc. However, even though the programs may adequately represent spatial relationships within the modelled system, other physical or chemical properties are unlikely to be described by the same programs. Further effort will be needed to achieve a link up between sets of routines describing pictures on the one hand and processes on the other. Computer capacity limitations also become a factor to be considered when such large programs are to be linked together.
2. In view of the issues mentioned in 1. it is reasonable to consider an approximate model as a basis for the study of a complete scientific problem by interactive graphics. Such models are characterised by a variety of parameters whose relationships can be usefully investigated through interactive graphics.
3. The procedure normally followed in scientific research

bears some formal analogy to the process used in computer aided design, (where graphics has been seen to be well established), as indicated in figure 2.1, and to other problem areas where solutions are derived from approximate models. Figure 2.1 also illustrates how a solution scheme for a complete problem analysis must allow for model testing and experimental validation before solutions are generated in production runs.

4. Through repeated interactive computer runs, it becomes possible to obtain a closer 'feel' for the problem and a better understanding of the solution procedure than when a conventional computing system is used. This is particularly so when the complete problem is approached by the use of a graphics system.
5. Model deficiencies, or errors in the modelling process, software errors and system design faults, where they exist, quickly become apparent when using interactive graphics.
6. The conventional procedure of analysing output, often produced at great length by a line printer, is substantially shortened and made more effective by well-designed graphics output facilities under selective user control. Suspected properties within the results can be investigated much more easily, and established relationships in the form of equations, or pictures of the curves themselves, may be retained, temporarily or permanently, to be used later on in the analytical process.


THE SCIENTIFIC APPROACH

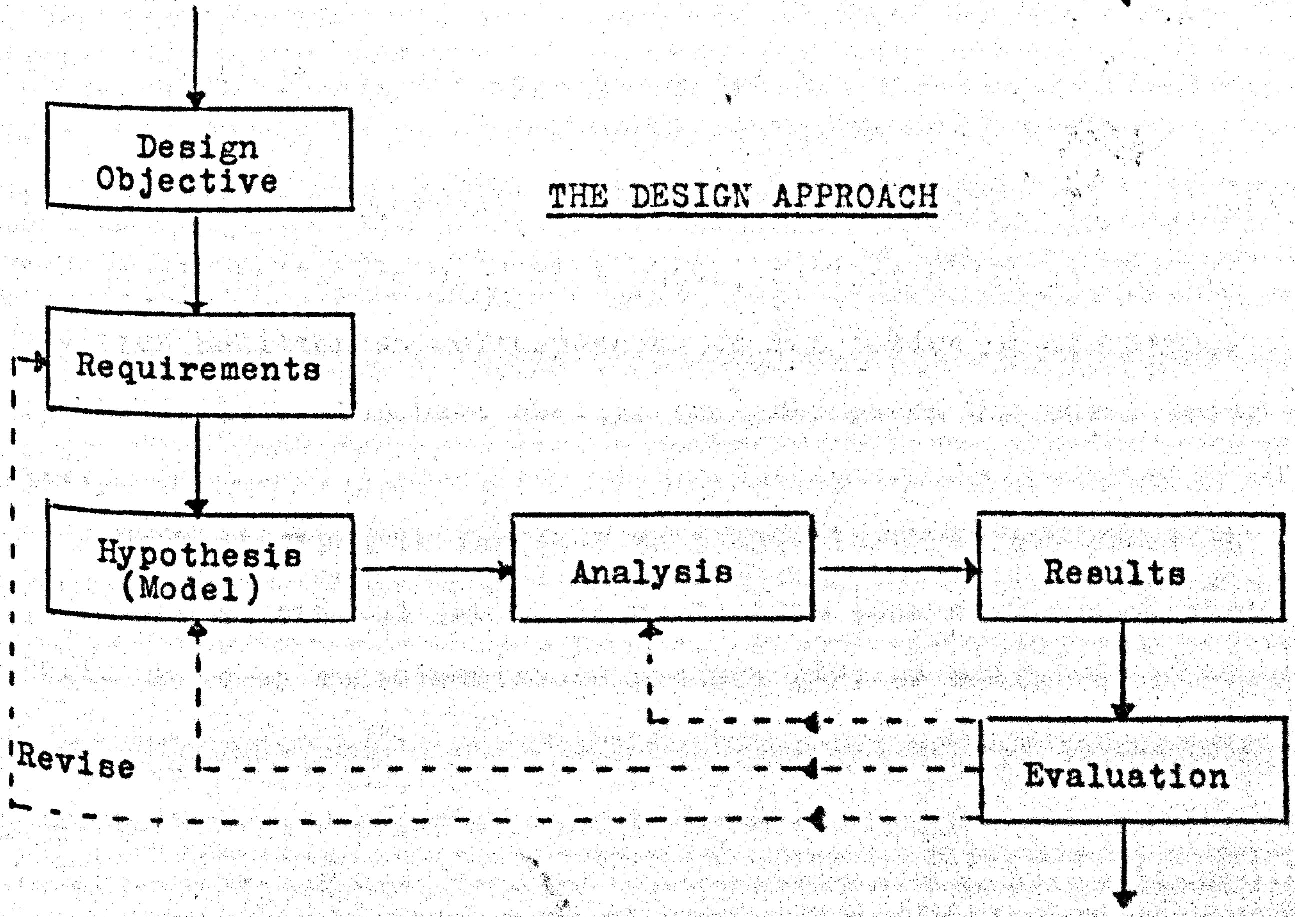

THE DESIGN APPROACH

Fig. 2.1

2.2 Quantum Chemistry Research

A brief theoretical statement of the general quantum chemical problem will now be given, together with an outline of the development of the self-consistent field molecular orbital method and, in particular, the approximate semi-empirical methods which relate to the discussion concerning the use of computer graphics.

The time-independent Schrodinger equation may be written

$$H\psi = E\psi \qquad -(1)$$

where H is the Hamiltonian operator for the electronic part of the system

$$H = \sum_i H^c(i) + \sum_{i<j} \frac{1}{r_{ij}} \qquad -(2)$$

where $$H^c(i) = -\tfrac{1}{2} \nabla_i^2 + V(i) \qquad -(3)$$

and $$V(i) = -\sum_I Z_I/r_{iI} = \sum_I V_I \qquad -(4)$$

(i and j denote electronic co-ordinates, I a nuclear co-ordinate, and atomic units are used throughout, so that $H^c(i)$ is the one electron Hamiltonian corresponding to the motion of electron i in the field of the bare nuclei, the charge on nucleus I being Z_I).

Each electron is assigned to a one-electron wave function or molecular orbital (MO). An n-electron wave function is then built up as an antisymmetrised product (AP) of MO's.

$$\Psi = (n!)^{-\frac{1}{2}} \begin{vmatrix} \psi_1(1)\psi_2(1) & \dots & \psi_n(1) \\ \psi_1(2)\psi_2(2) & \dots & \psi_n(2) \\ & & \\ \psi_1(n)\psi_2(n) & \dots & \psi_n(n) \end{vmatrix} \qquad -(5)$$

The MO's are products of a function depending on the space co-ordinates of the electron only and a function depending on the spin co-ordinates only, both functions being assumed to be orthonormal. The determinantal form of the wave function (5) then satisfies the antisymmetry principle, which requires the function to be antisymmetric to exchange of the co-ordinates of two electrons, and the Pauli principle, which implies that two MO's containing the same spatial function must have different spins. Such a pair of MO's is said to form a closed electron shell. A closed shell structure then refers to an AP completely composed of closed shells. Most molecules in the ground state have a closed shell structure in the MO approximation. Ground states will henceforth be described in terms of a single determinant, and excited states by single replacements of molecular orbitals used in constructing the ground state determinant.

The total electronic energy for the closed shell system is

$$E = \int\Psi^*H\Psi dv \qquad -(6)$$

This expression can be reduced to

$$E = 2\sum_i H_{ii} + \sum_i \sum_j (2J_{ij} - K_{ij}) \qquad -(7)$$

where $$H_{ii} = \int \psi_i^*(1)\, H^c(1) \psi_i(1) dv_1 \quad , \qquad -(8)$$

$$J_{ij} = \int \psi_i^*(1) \psi_j^*(2) \frac{1}{r_{12}} \psi_i(1) \psi_j(2) dv_1 dv_2, \qquad -(9)$$

and $$K_{ij} = \int \psi_i^*(1) \psi_j^*(2) \frac{1}{r_{12}} \psi_i(2) \psi_j(1) dv_1 dv_2 \qquad -(10)$$

are defined over space co-ordinates only. J_{ij} and K_{ij} are the coulomb and exchange integrals respectively.

According to the variation principle, the accurate solution of the many electron wave equation may be approached by varying all the contributing one-electron functions ψ_j in the determinant until the energy achieves its minimum value. The minimisation, which is carried out subject to the MO's remaining orthonormal, leads to the self-consistent or Hartree-Fock molecular orbitals, which give the closest possible approach to the correct many-electron wave function in the form of a single determinant.

The SCF molecular orbital, can be shown to be an eigenfunction of the Hartree-Fock operator F, so that

$$F\psi = E\psi \qquad -(11)$$

If the MO is expressed as a linear combination of atomic orbitals (LCAO)

$$\psi_i = \sum_{\mu} c_{\mu i}\, \phi_\mu \qquad -(12)$$

the nonlinear differential equations (11) are reduced to algebraic equations

$$\sum_{\nu} (F_{\mu\nu} - \varepsilon_i\, \delta_{\mu\nu})\, c_{\nu i} = 0 \qquad -(13)$$

generally known as the Roothaan equations. The matrix elements $F_{\mu\nu}$ are given by expressions first derived by Lennard-Jones, {10}, Hall, {11}, and Roothaan, {12}.

$$F_{\mu\nu} = H^{c}_{\mu\nu} + \sum_{\rho\sigma}\sum P_{\rho\sigma}\left\{(\mu\nu|\rho\sigma)-\tfrac{1}{2}\ (\mu\rho|\nu\sigma)\right\} \qquad -(14)$$

where
$$(\mu\nu|\rho\sigma) = \iint\phi_{\mu}{}^{*}(1)\phi_{\nu}{}^{*}(1)\ \frac{1}{r_{12}}\phi_{\rho}(2)\phi_{\sigma}(2)dv_{1}dv_{2} \qquad -(15)$$

and P is the bond order matrix with elements

$$P_{\rho\sigma} = 2\sum_{k} c_{k\rho}c_{k\sigma} \quad , \qquad -(16)$$

the summation k being taken over all occupied MO's ψ_{k}.

$$S_{\mu\nu} = \int\phi_{\mu}{}^{*}(1)\phi_{\nu}(1)dv_{1} \qquad -(17)$$

defines the overlap integral and the orbital energies ε_{i} are the roots of the determinantal equation

$$|F_{\mu\nu} - \varepsilon\ S_{\mu\nu}| = 0 \qquad -(18)$$

the lowest roots corresponding to occupied molecular orbitals.

In non empirical methods, the integrals involved in $F_{\mu\nu}$ are evaluated in terms of basis functions chosen to build up the adopted set of atomic orbitals ϕ_{μ}, whereas in semi-empirical methods, certain integrals may be given empirical values, and some may be neglected altogether.

Since $F_{\mu\nu}$ is dependent on the elements of P, the solution procedure for the coefficients $c_{\mu i}$ consists of first estimating the $c_{\mu i}$ to give an estimate of P which, in turn enables F to be constructed. The eigenvalue problem (11) is solved to yield an improved set of $c_{\mu i}$ and the process is repeated in this way until self-consistency is attained, thus giving final values for the required coefficients in the expression (12) for the ψ_i.

2.2.1 Computational Aspects

Since about 1950, research into the quantum theory of atomic and molecular structure has been assisted by the availability of the digital computer. Before this time, precise quantitative descriptions of molecular structures and chemical properties were possible in principle, but only the simplest systems, such as the helium atom, {16}, and the hydrogen molecule,{17}, could be studied in such detail, owing to the scale of the calculations involved. The underlying physical laws had long been understood in terms of quantum theory based on the Schrodinger equation, but the size of the computational problem for all but the simplest systems proved prohibitive until the advent of the electronic digital computer.

Computers are now used in two main and substantially different ways, namely

(i) in ab initio calculations, where all terms of the hamiltonian-operator are taken into account and all quantities needed are calculated explicitly, and

(ii) in approximate semi - empirical methods, where estimates, based on experiment or on numerical approximation, are made of quantities which are difficult to calculate and are therefore regarded as parameters of the approximate model.

Although the accuracy obtainable from ab initio calculations can, in principle, be increased without limit by extending the basis set and by configuration interaction (CI) methods, ab initio calculations are restricted by practical considerations to relatively simple molecules. The size of the basis set and the type of functions used are factors of particular computational significance. The functions themselves, in addition to exhibiting the correct general behaviour, must lead to integrals that can be evaluated, and the number of functions that may be used is limited by the available capacity for calculating, storing and manipulating all the required integrals. Despite the practical difficulties, high accuracy as compared with experiment can be obtained, often by choosing a fairly extensive basis set and then being very selective in the configurations retained.

Larger molecular systems can be studied by recourse to approximate methods, in which standard mathematical techniques and statements of the problem e.g. the Schrodinger equation, are used - but these are applied to models of the physical system. Essentially, terms corresponding to the total hamiltonian are combined together to produce an approximate operator which applies, in effect to a parameterised model of the system. Although the nature of the simplification is fairly well understood in terms of the complete mathematical description, the overall numerical magnitudes of the approximations are seldom measurable. Physical plausibility of the model, coupled with an understanding of the nature of the approximations, enables the parameters to be chosen with some justification. Agreement between predicted results and those obtained experimentally must be established to provide an acceptable model, but since parameters of the model are themselves usually chosen by appeal to other experimental observations, there is some degree of insurance of success built into the design of approximate semi-empirical methods. However, they must at least display a consistent pattern when applied to many different molecular species. The size of molecule which can be studied using approximate methods depends on both the degree of approximation adopted in the theoretical model and the size of computer used. The accuracy of the solutions obtained relative to ab initio or experimental results will depend on the effectiveness of the parameterisation and on the values given to the individual parameters,

The project described in this thesis is not concerned with ab initio calculations. It would be both possible and interesting to use a graphical display device to examine experimentally the properties of solutions arising from such calculations. However, the solutions themselves would all need to be computed beforehand and recorded on some form of backing store, since the calculations involved are, in general, too lengthy to be considered in an interactive context. The purpose of the interactive graphics system discussed here calls for a more flexible system with greater variety of application than that provided by ab initio calculations, which at most could be handled graphically in the initial and final phases of the project as discussed in section 2.1.

Semi-empirical methods will form the focus of attention from now on. In particular, these methods applied to π electron systems offer great variation in scope, and illustrate extremely well the capabilities of interactive computer graphics in the study of the different phases, and indeed all the phases of the problem in this field of quantum chemistry.

It is recognised that there is less scope here for the development of new theories or results than in the ab initio field, for example, since most of the major problems in the chosen field have already received sufficient attention elsewhere. However, it is probably advantageous that this is so, because the established procedures and solutions provide criteria for testing the project in practice and, furthermore, to some extent they point the way to system design

2.2.2 Analysis of the π-electron Systems

The SCF-MO method, in the LCAO form described above, allows all electrons in the system to be specifically taken into account. A further approximation considers the π electron system to be moving separately in a constant σ-bonded framework - an assumption based upon empirical evidence which suggests that chemical properties of conjugated molecules may be ascribed to the π electrons alone. The methods within this approximation differ in the way in which the integrals in $F_{\mu\nu}$ are treated. Two such methods, which will later be used in the interactive graphics system, will now be described.

2.2.2(a) The Pariser-Parr-Pople (P-P-P) method

This method originated in work by Pople {13} and by Pariser and Parr {14,15}, and falls within the category of zero-differential overlap (ZDO) approximations.

All $S_{\mu\nu}$ and $H^c_{\mu\nu}$ integrals between non-neighbouring conjugated atoms are ignored and, for consistency, all electron-repulsion integrals depending on the overlap of charge clouds are also ignored.

The two-suffix terms

$$(\mu\mu|\nu\nu) = \gamma_{\mu\nu} \qquad -(19)$$

remain non-zero, enabling the off-diagonal elements of the hamiltonian operator h for the system of n π electrons to be derived from (14) in the form

$$h_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2} P_{\mu\mu} \gamma_{\mu\nu} \qquad -(20)$$

with the core matrix element given by

$$\beta_{\mu\nu} = h^{c}_{\mu\nu} = \int \phi_{\mu}{}^{*}(1)(-\tfrac{1}{2}\nabla_1^2 + V_{\mu} + V_{\nu})\phi_{\nu}(1)dv_1 \qquad -(21)$$

when potentials of cores distant from nuclear centres μ and ν are ignored.

The diagonal elements of h may be written

$$h_{\mu\mu} = h^{c}_{\mu\mu} + \sum_{\nu} P_{\nu\nu}\gamma_{\mu\nu} - \tfrac{1}{2} P_{\mu\mu}\gamma_{\mu\mu} \qquad -(22)$$

with the core matrix element given by

$$h^{c}_{\mu\mu} = \omega_{\mu} + \sum_{\nu\neq\mu} \int \phi_{\mu}{}^{*}(1)V_{\nu}\phi_{\mu}(1)dv_1 \qquad -(23)$$

where

$$\omega_{\mu} = \int \phi_{\mu}{}^{*}(1)(-\tfrac{1}{2}\nabla^2 + V_{\mu})\ \phi_{\mu}(1)dv_1 \qquad -(24)$$

refers to the framework ion μ only.

Therefore

$$h_{\mu\mu} = \omega_{\mu} + \tfrac{1}{2}P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\nu\neq\mu} (P_{\nu\nu}\gamma_{\mu\nu} - \int \phi_{\mu}{}^{*}(1)V_{\nu}\phi_{\mu}(1)dv_1) \qquad -(25)$$

If the nuclear centres associated with μ and ν are far apart, the integrals

$$\int \phi_{\mu}{}^{*}(1)V_{\nu}\ \phi_{\mu}(1)dv_1 \quad \text{and} \quad \gamma_{\mu\nu}$$

may be approximated by the inverse distance law, so that

$$P_{\nu\nu}\gamma_{\mu\nu} - \int \phi_{\mu}{}^{*}(1)V_{\nu}\ \phi_{\mu}(1)dv_1 = (P_{\nu\nu} - Z_{\nu})r_{\mu\nu}^{-1} \qquad -(26)$$

where Z_{ν} is the effective, screened, charge at the framework ion ν.

Since the $\gamma_{\mu\nu}$ are regarded as adjustable parameters, it is permissible to write

$$P_{\nu\nu}\gamma_{\mu\nu} - \int\phi_{\mu}^{*}(1)V_{\nu}\ \phi_{\mu}(1)dv_{1} = (P_{\nu\nu} - Z_{\nu})\ \gamma_{\mu\nu} \qquad -(27)$$

giving a final form for the elements of h, namely

$$h_{\mu\mu} = \omega_{\mu} + \tfrac{1}{2}\ P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\nu\neq\mu} (P_{\nu\nu} - Z_{\nu})\ \gamma_{\mu\nu} \qquad -(28)$$

$$h_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \qquad -(29)$$

which, with Roothaan's equations (13) reduced and re-written in the form

$$\sum_{\nu} h_{\mu\nu}\ c_{\nu i} = \varepsilon_{i}c_{\mu i} \qquad -(30)$$

define the SCF equations for π electron systems in the P P P approximation.

2.2.2(b) The Huckel MO Method

The Huckel method within the π electron approximation has been successful in explaining many properties of organic molecules. However, this simple theory does possess several unsatisfactory features, the recognition of which has led in part to the development of more recent theories of somewhat greater sophistication.

Nevertheless, it is included here because, even at this level of approximation, models and solutions for certain molecular systems possess properties which can be effectively analysed with the aid of interactive graphics.

An effective hamiltonian operator h which does not treat inter-electron repulsions specifically is adopted. The matrix elements are assumed to be meaningful quantities, all of which may be given empirical values, so that

$$h_{\mu\nu} = \beta_{\mu\nu} = \int \phi_\mu{}^*(1) h\, \phi_\nu(1) dv_1, (\mu, \nu \text{ neighbours})$$

$$= 0 , (\mu, \nu \text{ non-neighbours}) \qquad -(31)$$

and $$h_{\mu\mu} = \alpha_\mu = \int \phi_\mu{}^*(1) h\, \phi_\mu(1) dv_1, \qquad -(32)$$

where $\beta_{\mu\nu}$ and α_μ are known as the resonance and coulomb integrals, respectively.

The secular equations then take the form

$$(\alpha_\mu - \varepsilon_i)c_{\mu i} + \sum_\nu \beta_{\mu\nu} c_{\nu i} = 0 \qquad -(33)$$

and may be solved by equating the corresponding secular determinant to zero, and solving for the allowed energies ε , which can be substituted in (33) to give the required coefficients.

- - - - - - - - - - -

The π electron approximation presents two main problem areas which may be studied effectively using interactive computer graphics.

The first is concerned with the problem of establishing the best choice of parameters e.g. α_μ, $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$, ω_μ etc, to fulfil a given purpose, and the second problem area is the investigation of analytical relationships inherent in the approximate models.

The methods described above, and variations based upon them, have been successfully applied to a wide range of chemical problems. Much of the success, particularly of the P-P-P method, is due to the effect of the empirically chosen parameters which can compensate for errors arising out of the ZDO approximation. However, difficulty has been experienced with this method in obtaining one set of parameters which can usefully serve in the description of both ground state and spectroscopic properties. Studies have tended to be concentrated in restricted areas, leading to parameter definitions which have produced good agreement with experiment or with ab initio calculations in the specific area, but which have proved less satisfactory when applied more generally. There is scope for an extended study to evaluate the relative merits of different parameterisation schemes over a wide range of molecular systems. Such a study could proceed most effectively through the use of interactive computer graphics. Exactly how graphics is able to contribute in this problem area will be discussed in the next section, and some experiments in the use of a graphics system with alternative parameterisation schemes will be described in a later chapter. It should, however, be stressed that these experiments in no way represent the extensive study needed to arrive at firm conclusions regarding the relative merits of the individual schemes used.

The SCF equations, unlike the Huckel equations, are nonlinear in the coefficients that define the solutions. This makes it more difficult to deduce analytical properties of the SCF model. However, it is often possible to demonstrate numerically the existence of such properties, using computer solutions, and this can be an important step towards establishing theoretical proofs of properties having both chemical and computational significance.

For instance, Greenwood and Hayward, {18}, deduced analytical properties describing parametric variations about solutions for parent even alternant hydrocarbons in the SCF model. The properties are very similar to analagous properties in the Huckel model, and explain, in part, its success in describing ground state properties, despite the explicit neglect of inter-electron repulsion terms. Recognition of these properties also permits economies to be made when planning computer runs.

Interactive computer graphics can offer considerable assistance in this type of numerical investigation of the properties of solutions. Variations in solutions or in quantities derived from the solutions may be observed and quantitatively established in relation to selected parameter variations. Experiments in the application of a graphics system in this problem area will also be described in a later chapter.

2.3 Semi-empirical Methods as an Application Area for Interactive Graphics

In this section, the reasons for choosing the semi-empirical methods of quantum chemistry research as an appropriate area within which to study interactive graphical computing techniques are considered in greater detail. In particular, the section identifies procedures in the application of such methods which can be regarded as typifying the various phases of the general scientific project where interactive graphics can be used for both control and analysis.

The overall aim, however, is to investigate the feasibility of using interactive computer graphics to control a complete scientific project - from the initial model specification, through the analysis of model solutions, to the production of the final results.

The semi-empirical methods determine a problem solving procedure which is well structured from the interactive control point of view. The methods are based on analytical models, at varying levels of approximation, which can be specified interactively, and whose solutions can generally be computed and displayed within a brief enough space of time to be considered reasonable in an interactive setting. Also, each stage of the procedure gives rise to visual information which can be analysed, and used to determine subsequent activities under user control. A system can, therefore, be devised, which gives the user control, via the graphics display unit, both of the processes within the individual stages and of the overall sequence in which the stages of the project are performed.

The stages typically involved in an interactively controlled semi-empirical quantum chemistry experiment will now be outlined, and for each stage an indication will be given of how graphical facilities can be used to advantage.

The first step in such an experiment is to identify the molecule which is to form the basis of the study. This can be done in different ways using interactive graphics.

One way is to first of all generate a geometrical image of the molecule on the display screen, and to program the system to recognise the atomic positions for subsequent use in the calculations. For example, the carbon atoms in a hydrocarbon molecule can be picked out, one by one, using the light pen, from a displayed hexagonal grid. Once the molecular geometry has been established, individual atom replacements e.g. of C by N, can be made by re-tracing the molecule and indicating the type of replacement at each position. This indication is made by inputting data in accordance with a displayed key, and the system can be programmed to take account of the modifications in the calculation stage. The picture of the molecule can be retained and may be recalled for reference at any point in the analytical part of the project, or it can be used to indicate further modifications prior to a new calculation.

Another way of identifying the molecule is to refer to a displayed list of named molecules, details of which are already available on backing store. Such details can range from a simple geometrical definition which could be used to initiate calculations, to a catalogue of computed, stored solutions which can be used for analytical purposes. Further displays indicate exactly what is available to the user. This type of approach is sometimes useful when larger molecules are being studied, since the selection process mentioned above or some fairly lengthy calculations can be by-passed if desired.

Having identified the molecule, the next step is the selection of the method, or model, to be used in the analysis, e.g. Huckel, SCF, SCF-CI etc. This may be achieved by making a selection from a displayed list of named methods, using the light pen or some alternative device.

Associated with each method are certain parameter requirements which can be fulfilled in a number of ways. The individual parameters which have to be specified, followed by the alternative parameterisation schemes currently available for each one, can now be displayed. The user selects a scheme from the displayed lists, and this results in parameter values being set automatically for the molecule as defined earlier. Alternatively, by recalling the displayed molecular image, the user can nominate individual atoms or bonds using the light pen and input numerical values for the indicated parameters.

When these operations are complete, the mathematical model, in the form of matrix elements and equations, is fully determined, and, on a signal from the user, the calculation of the wave functions and associated energy levels begins.

The basic ground state solution can be effectively displayed using graphical techniques. The familiar but useful diagrams showing energy levels as a set of short horizontal lines positioned on a vertical energy scale can be displayed singly or, when comparing a group of solutions arising due to parameter variation, the diagrams can be displayed simultaneously, side by side. A suitable diagrammatic representation of a molecular orbital depicts the contributions of the atomic orbitals in the LCAO formulation as short vertical lines based at equal intervals along a horizontal axis. The length of each vertical line is proportional to the magnitude of the coefficient which it represents, and it lies above or below the horizontal line according to the algebraic sign of the coefficient. All of the diagrams are completed by the inclusion of appropriate numerical information for reference purposes.

Quantities to be derived from the ground state solution, such as charge densities, bond orders, dipole moments etc, can be selected from a list, and computed as a complete set, or as individual items specifically requested by the user; for example, by nominating an atom, either with the light pen on the diagram or by input of the atom number in order to initiate a charge density calculation.

The components of a CI solution also offer scope for good graphical displays. The individual state energies relative to the ground state can be displayed in a single diagram, or collected as a set of diagrams, demonstrating the variation with model parameters, in a similar way to that described above for ground state energies. The state wave-functions can be displayed in a similar manner to that used for ground state molecular orbitals where here the vertical lines represent contributions of different configurations.

Individual oscillator strengths which relate to transition energies can be computed and then displayed in a diagrammatic form which represents the spectrum. The oscillator strengths are depicted by vertical bars of proportionate length rising out of a horizontal 'energy' axis. These diagrams can be effectively combined, one above the other, to demonstrate the effects of parameter variation on both intensities and energies.

Over and above the qualitative demonstration of variations with respect to model parameters provided by all these diagrams, a firmer indication of relationships may be obtained by submitting observations taken from the diagrams as data to the curve fitting and graph plotting section of the program. Individual items e.g. energy, intensity etc, can be nominated by input of the appropriate numerical control data in accordance with displayed instructions appearing alongside the diagram from which selections are to be made. The type of curve fitting operation will be selected from a list of those available, and the user is also able to specify the degree of curve required. Other features of value at this stage include optional manual scaling facilities for better presentation of curves, transformation of variables, multiple curve display facilities for comparison purposes and hard copy graph plotting facilities whenever required.

The stages of the project, as outlined above, collectively form the typical phases which are generally regarded as being part of the scientific approach to problem solving, namely problem definition, model formulation, calculation and analysis of solutions. Interactive computer graphics can make useful contributions within these phases in many applications of the 'scientific approach'. However, the semi-empirical methods of quantum chemistry present particularly well defined phases, within which, as seen above, there is ample material for graphical display, analysis and control decisions. Hence the chosen problem area is especially suitable for demonstrating how an interactive graphics system can be developed for controlling a scientific project in all its phases.

2.4 Design of a Graphics System for use with Semi Empirical Methods

Consideration is now given to the more practical issues that arise in the design of a graphics system for use in studying problems which can be investigated with semi-empirical methods of quantum chemistry. Some general principles of design for interactive computer graphics were discussed in the first chapter, but each new project calls for an examination of these principles in relation to the particular needs of the new application.

The five main design aspects to which consideration must be given are

(i) program structure and control

(ii) interactively controlled calculations - to determine what, if anything, should be computed

(iii) storage allocation - what needs to be stored, temporarily or permanently, in relation to processing

(iv) displayed information - the volume presented by each display

(v) analytical processing - what facilities are required.

The decisions made in connection with these five points depend to a large extent on the hardware and software facilities available, but, within the existing limitations, decisions must still be made which will have a significant effect on the ultimate performance of the interactive system.

The points at issue will now be considered in relation to the design of a system specifically intended for use with semi-empirical methods.

2.4.1 Program Structure and Control

It was seen in the previous section that the problem solving methods under discussion can be broken down into readily identifiable phases. A comparable structuring of the overall interactive program is desirable because

(i) a modular approach facilitates program development, both in the early stages, and later when extensions to the system are introduced,

(ii) core storage economics through overlaying and segmentation are more easily effected,

(iii) with well defined program phases, overall user control is easier to organise and simpler to operate in practice. Free 'movement' between phases, essential when the scientific approach is followed, can also be achieved,

Control information, indicating how to proceed to the next stage in the program or how to transfer to another stage must be displayed on the screen, consistently and unambiguously. An extra user action, which confirms a command before it is obeyed, is usefully included, since it helps to avoid accidental initiation of lengthy calculations such as SCF procedures. A backtracking mechanism, enabling a previously held position to be recovered in case of error is also valuable.

2.4.2 Interactively Controlled Calculations

A conventional SCF procedure consists of several cycles of a sequence of operations - generation of the SCF matrix followed by a matrix diagonalisation. The time taken depends upon the size of the matrix, the number of iterations needed to attain self-consistency and, of course, the speed of the computer used. In the case of the ICL 4130 computer, used in the practical system to be described later, the time taken to obtain SCF solutions for naphthalene, for instance, is around twenty seconds, which is clearly acceptable in the interactive sense. Response times of up to two or three minutes may be acceptable in practice. Using graphics interactively is not comparable with interactive programming through conversational languages, where response times of ten seconds are usually considered to be unacceptable. In any case, displays often contain so much information that the user may take longer than a minute to digest the results before making the next move.

In these circumstances, SCF procedures can justifiably be incorporated into the overall system, and by a similar token CI routines and of course Huckel routines may be included. The computation of derived quantities can in most cases be accomplished in less than one second, so the appropriate routines should be provided in the system.

2.4.3 Storage Allocation

When the solution calculation procedures are included in the system, two types of interactive computing session can be envisaged. First, there will be sessions wherein sets of interrelated solutions will be computed, under the control of the user, and permanently stored to await subsequent analysis. In certain circumstances, when for example, larger calculations are involved, it may be necessary to compute solutions off-line. In the second type of session, analysis of solutions takes up most of the time, and this is based mainly on previously computed and stored solutions, with occasional computation of a new solution to confirm or extend the analysis.

Thus there is a need for storage to be allocated on backing store for ground state solutions, consisting of energy levels and molecular orbitals, together with details for each solution of the parent molecules, parameter values and the type of solution e.g. Huckel, SCF etc. These details form entries in a catalogue of the stored solutions which must be available to the user via the display. On the user's making a selection from the catalogue, the chosen solution will be brought into core for display, analysis or further processing. Similarly, the user must be able to add solutions to the library or replace them, and make corresponding amendments to the catalogue.

A particular investigation in depth of some problem may require additional permanent storage to be reserved. For instance a set of CI solutions could be assembled for analytical purposes and stored permanently to avoid the need to re-compute them if the analysis extends over more than one interactive session.

Adequate provision must also be made within the program for temporary storage, in the form of core buffers, of selected solutions, derived quantities and analytical results, so that within a single interactive session graphical comparisons may be made between selected experimental results. However, strict economy must be practiced in the design, since many other demands on core storage space exist in a graphics system.

2.4.4 Displayed Information

The question of how much information is presented to the user via the graphical display is fundamental to the design of a graphics system. The information displayed can serve several purposes. In addition to the control information already dealt with, a wide range of material for analytical purposes is available in the current application area. Models, data, solutions and curves must all be displayed neatly and consistently. Textual material must use terminology and language which relate to the quantum chemistry problem and to computing procedures, and which are chosen to avoid confusion. Each display must be concise enough to enable the user to fully comprehend the information it contains, and to make a decision on the next move within a minute, or two at most. Results which are to be plotted as a permanent record should be fully annotated for future reference and precise enough for publication.

2.4.5 Analytical Processing

Curve fitting routines and data and curve manipulation routines are available. Sometimes the data sets generated possess symmetry of some kind, and storage space and computing time can be conserved by generating only part of the data, from which image points may be derived. Data points may be selectively removed temporarily from a displayed set, and a curve fitted through the remainder. Horizontal and vertical translations of curves are useful when comparisons are to be made or when an origin shift takes place, and more general transformations of variables can be made. Automatic scaling and drawing of axes is normally achieved by the use of standard software. However, these routines are sometimes found to exaggerate the shapes of curves or to present difficulties when several curves are to be displayed simultaneously. For instance, the scales and axes automatically calculated for one curve may result in a second curve being partially or wholly omitted from the display screen. A manual over-ride of these automatic functions must therefore be included.

A practical implementation of these design considerations is described in detail in the next chapter. The modular flexible approach taken has already enabled improvements and extensions to be made, and permits further modifications such as may be suggested by practical experience with the working system. The system is presented, therefore, as an on-going experiment in the use of interactive computer graphics for control and analysis within all the stages of a complete scientific project.

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CHAPTER THREE

A GRAPHICS SYSTEM FOR QUANTUM CHEMISTRY RESEARCH

In the previous chapter some basic requirements of research work in quantum chemistry were discussed in relation to computing procedures, and indications were given suggesting how interactive computer graphics might be of assistance in the various aspects of this type of work. Some specific factors concerning the design of a graphics system for use with quantum chemistry were also considered.

In this chapter a comprehensive program (MOANAL) written in FORTRAN for an ICL 4130 computer with a graphical display unit is presented. The design of the program follows many of the prescriptions identified and discussed in the earlier chapter. In particular, the program is designed to possess four essential attributes -

(i) it is straightforward in use,
(ii) response times are short,
(iii) adequate automatic storage facilities are incorporated,
(iv) it has flexibility for adaptation and extension.

The chapter begins with a section presenting an overall view of the graphics system. This introductory section outlines, under separate headings, hardware mechanisms that are available for interactive communication with a program, and software features arising in the design of graphics programs. It also combines and relates these aspects to operational procedures.

The design aims and structural details of the system are related to a 'menu' type of program which is used within a man/machine communication environment based on the graphical display to initiate and control computing activities. Essentially the program consists of a set of levels or stages linked in an ordered sequence corresponding to the processing sequence. Within each stage are several states, representing decision points at which the user interacts to initiate the next step in the program. The options at each such state of the program are displayed in the form of a 'menu' consisting of a set of numbered 'menu items'. Each item corresponds to an instruction in the program which is obeyed when the item is selected. On completion of the instruction, an automatic transfer is made to another state, possibly in a different stage. The location of the destination state will depend upon the logical position of the prior state and the decision made by the user.

This form of control relates both to display techniques used in computer graphics and to the structure of the problem to be studied. Like many scientific problems, the treatment and organisation of the problem-solving procedures that arise within the approximation methods of quantum chemistry can be broken down into well-defined modules, phases or levels. The program structure has, therefore, been designed around a formal hierarchichal problem solving scheme of this kind. Four such levels have been established in the present case. They are:

1. Identification of the system to be studied, i.e. selection of molecules.

2. Choice of model, e.g. Huckel, various SCF-CI schemes.
3. Examination of solutions.
4. Analysis and transformations of solutions.

Usually several states of the program are associated with each problem-solving level, each state having its associated display 'frame' which may show, for example, the menu of options, diagrams or curves and certain other basic commands whose functions will be described in a later section.

Details of the existing states and options available to the user in each of the four levels of the program are given in separate sections of the chapter, following on the overview section. These sections also include descriptions of the important display and analysis subroutines which are used in the corresponding levels of the program. A final section gives an account of the procedures adopted for storage and retrieval of data representing either solutions to problems or information appearing on display frames.

3.1 Overview of the Graphics System

One of the first questions to be decided when creating a graphics system is the choice of programming language to be adopted. Some of the languages which have been used in various applications, together with their advantages and disadvantages were discussed in chapter one. Here, the main program and the accompanying subroutines are written in FORTRAN. The reasons for arriving at this choice will now be given.

It is acknowledged that there are certain disadvantages in using FORTRAN for a graphics program of this type. In particular it is expensive on core space compared with low-level languages and is cumbersome as a means of programming the branching procedures which arise extensively in computer graphics. This latter difficulty manifests itself in the countless "IF" and "GO TO" statements which appear within the graphics program. However, both disadvantages can be overcome to some extent by practising economy in programming and by careful management of core allocation in which one endeavours to hold in core at any time only those data and subprograms currently required. The division of the main program into four levels of operation, as discussed above, and the simultaneous use of the segmentation facility with subroutines assisted in making the present program modular and compact in structure and efficient in processing.

The advantages which were considered to more than offset such disadvantages in using FORTRAN were -

(i) the flexibility to incorporate existing FORTRAN subprograms for quantum chemistry. Use may be made of adapted versions of existing programs for both Huckel and SCF-CI semi-empirical methods for both π and σ electron systems [1,2]. Some problems invariably arise in restructuring programs to satisfy, for example, core restrictions, but the organisation of the graphics system itself has been designed so that extensions to the list of available models can be incorporated with comparative ease.

(ii) the potential for incorporating additional subprograms to perform specific functions. These may be seen to be required as an investigation in a particular area of application deepens, possibly extending the analysis of solutions or involving the introduction of new theoretical procedures.

(iii) the availability of a graphical package of FORTRAN subroutines, DISPAC, {4}, as described in Appendix A, which has been derived at Keele University from ICL graphical software, {5}. The package facilitates the programming of interactions and the organisation of textual, numerical and graphical information for the display screen. Despite being fairly expensive in terms of core space, DISPAC makes for much more effective communication with the 4280 display unit, which is described in Reference {5}. Economy of core space can be achieved by confining usage at any one time to a subset of the package.

(iv) the transferring of the programs to another computer should be feasible, requiring comparatively little support programming. It would be a matter of replacing the DISPAC functions corresponding to their respective CALL statements by similar functions for use by the second computer. It is likely that backing store procedures would also require some attention. Some optimism for effecting such transfers, based on experiences with a FORTRAN program and a 4280 display used for process plant design has been expressed by Daniel, {6}.

The advantages outlined above, together with a careful consideration of the type of problem which is to be solved led, therefore, to the choice of FORTRAN for the programming language.

A second important factor having considerable influence on the overall design of the system is the user. He will not necessarily be the same person as the programmer of the system. It is vital, therefore, that a clear idea is obtained at the outset of what the user requires of the system and, conversely, of what the system demands of the user.

In many existing graphics systems, various degrees of explanation are available as options to the user at certain decision points in the program. The more elementary forms of explanation are intended as an aid for the new or inexperienced user. These are considered largely unnecessary in the context of the present work, since it must be assumed, in graphics applications associated with scientific research, that the user is reasonably well versed in the problem solving process. By carefully ensuring that all the names, messages, instructions and option labels appearing on the display screen are compatible with quantum chemistry terminology and as such are immediately recognisable to the user, the extra programming problems and the additional storage space which these elementary explanatory facilities would require are avoided. A backtracking facility and a decision confirmation procedure are, however, built into the present system to protect the user against his own inevitable processing errors.

As suggested above, the user is expected to be familiar with fundamental procedures and terminology of quantum chemistry and, preferably, to have some experience of batch type molecular orbital computer calculations. The program will then be found to offer a rapid and effective means of undertaking analysis of the properties of molecular models with several interesting degrees of variation and sophistication. It is perhaps worth indicating at this point that although the dialogue and options currently available are not specifically designed for the newcomer to quantum chemistry, the system possesses flexibility for modification and adaptation along lines which would give it considerable value as a teaching aid.

3.1.1 Hardware Mechanisms

User interaction with the 4280 graphical display unit (shown in Figure 3.1) may be accomplished by three different means, namely -

(i) the eight numbered keys on the display console itself. These may be individually examined for being in the on or off state at any desired point in the program. A mechanism is available whereby the execution of the program may be delayed until a key is switched on. The next step taken in the program will depend upon which key is chosen, it being usual to arrange for a list of key numbers and their corresponding meanings to be displayed on the screen at the appropriate time. In effect, the user is given a means of inputting as symbolic data to the program any integer from one to eight, or even more numbers if combinations of the keys are used.

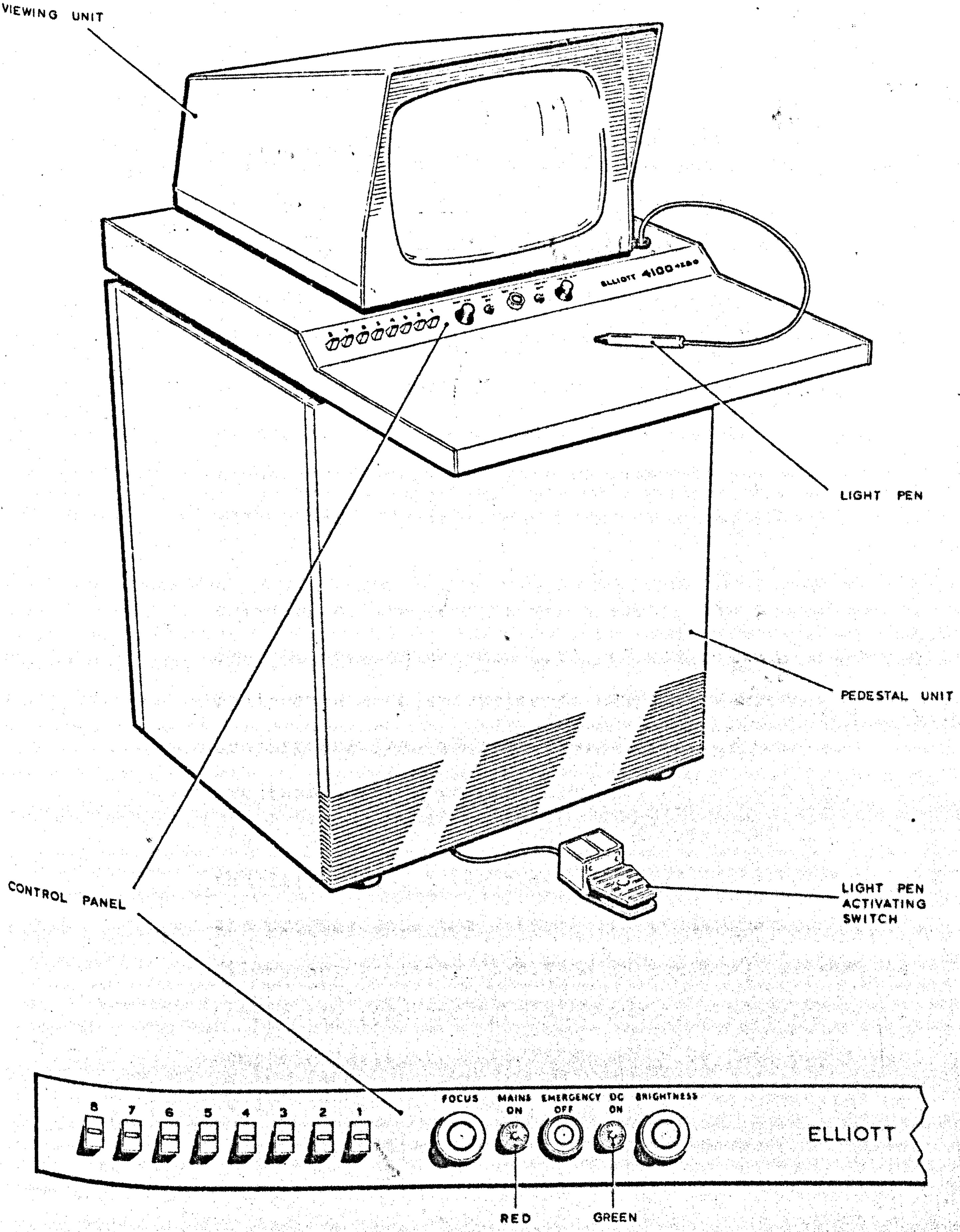


Fig. 3.1

DISPLAY UNIT & CONTROLS

Figure 1 ISSUE [illegible]

(ii) the light pen, which is placed against the screen and activated by pressing a foot switch. This may be used in three ways:-

(a) the mechanism can be programmed to return the actual x and y co-ordinates of the tip of the pen at the instant of activation. This feature is useful when a particular point such as a data point, or an area of the screen which will be identified by a point in that area, needs to be indicated.

(b) the picture is built up, part-by-part in display 'items' by entering numbered, coded pieces of information corresponding to display items into the display file. Code for items may be added to or taken from the display file, causing a parallel appearance or deletion of the item on the screen. The programmer is free to determine which parts of the picture are to be designated as display items; the entire picture could be just one item if required. The light pen can be programmed to 'recognise' an item on the screen. In other words this means that the identifying number of the item at which the pen is pointed is returned to the program once the foot switch is depressed. This allows any piece of displayed information, ranging in complexity from a single alphanumeric character to a complete curve, to be referenced. The item may then be deleted, modified, moved or otherwise processed as a complete entity, independently of the rest of the picture.

(c) for more accurate indication of points a tracking cross may be programmed to appear on the screen. This will follow the activated light pen to any desired position on the screen. Once in place the co-ordinates of the centre of the cross can be returned to the program, possibly on switching a specified key in the manner described in (i) above.

(iii) the 'teletype' keyboard which is a valuable facility enabling either textual or numerical information to be entered. In the present context this is most likely to be used for entry of names of molecules or titles of curves etc., chosen by the user for incorporation at run time. Both numerical floating point and integer data can also be input at run time in this way. A floating point number would typically be entered as an independent variable from which the program might be expected to calculate a related quantity, as a scaling factor or as the extent of a linear transformation which is to take place. An integer could be entered to indicate the number of an energy level for which a plot is required against some previously specified modification or to initiate some infrequently used operation such as a jump back to the start of the program. For instance a message may be displayed requesting the user to type '99' if the current piece of analysis is to be abandoned.

It is of course also possible to program the system to read pre-prepared data from cards or tape. The actual reading operation would be preceded by a displayed message requesting that the data be loaded into the reading device and indicating which interaction mechanism will initiate the physical reading of the data. The facility is especially useful at the program design or extension stages, when both literal and quantitative data of known accuracy can be used for test purposes. Display routines and numerical subprograms and processes can thus be examined for accuracy and speed of execution.

3.1.2 Software Design

As indicated earlier, the graphics system is designed in terms of a menu type of structure for interactive control of processing through the display. The breakdown of the quantum chemistry problem into four main phases or levels, each having recognisable sequences of processing modules is reflected in the design of the overall structure of the system. At the same time the interactive operations that appear on the display frames as individual menu items or options available to the user at different levels relate to the various hardware mechanisms for user interaction with the processing procedures. Thus hardware and basic software considerations, together with a close examination of the nature of the problem and the purpose of the analysis, combine to suggest the structure of the program and the mode of dialogue to be employed. The FORTRAN call to MENU, the relevant subroutine with its list of arguments, provides an intuitive guide and a symbolic summary of its central role within the computer graphics system. Thus

```
    CALL MENU (NW,WORDS,KWORD,LEVEL,NXTER,MOD,NBUFF)
```

where the variables have the following meaning:-

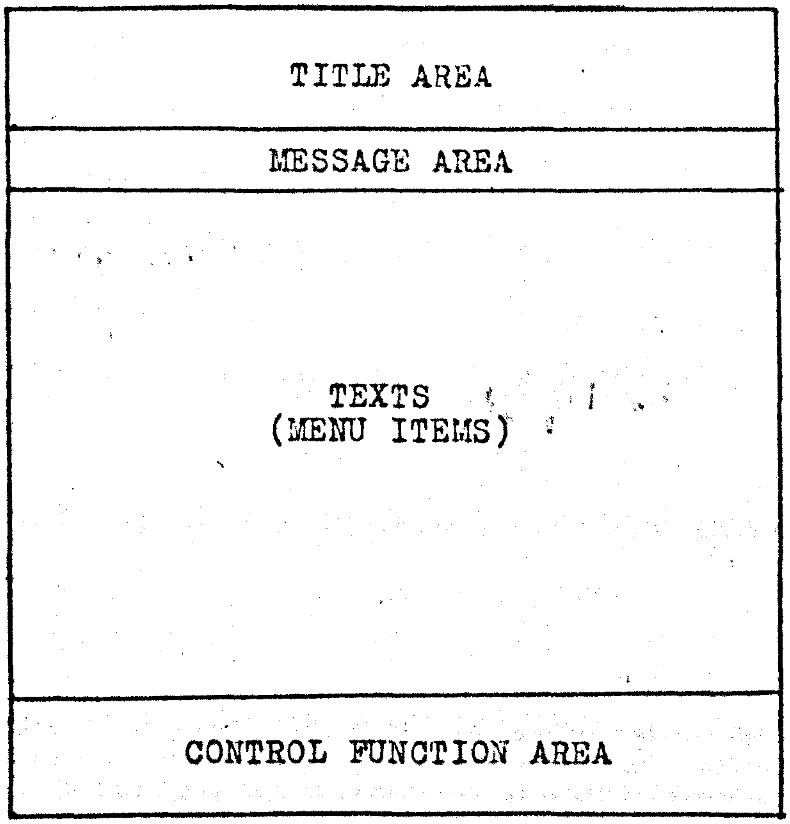

TITLE AREA
MESSAGE AREA
TEXTS
(MENU ITEMS)
CONTROL FUNCTION AREA

Fig. 3.2

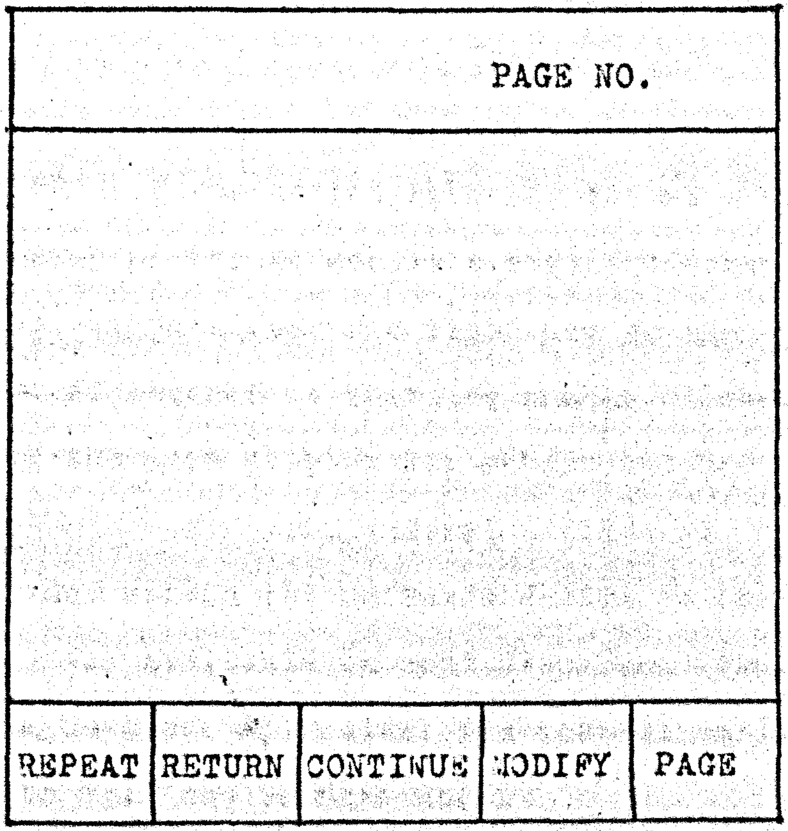

PAGE NO.
REPEAT
RETURN
CONTINUE
MODIFY
PAGE

Fig. 3.3

NW - number of menu items in the current menu,

WORDS - array containing the menu items and display title,

KWORD - number of selected menu items, used to control branching,

LEVEL - indicates the level of the main program,

NXTFR - frame number in the current level,

MOD - set equal to the number of a modified menu item or to zero if no modifications are made,

NBUFF - array acting as code buffer for information to be entered into the display file and hence to be displayed.

A flow diagram of subroutine MENU is given in figure 3.4. The subroutine is entered with a menu of options (menu items) and the title of the menu contained in the array WORDS. The number of menu items in the menu, and the current level of the main program are indicated by NW and LEVEL respectively. The display frames have a consistent breakdown into areas with separate functions as shown in figure 3.2. The frames within each level of the main program are given a reference number which is identified with NXTFR. If the action taken by the user whilst the menu is displayed on the screen is a straightforward selection of a menu item, using either the light pen or the console keys, then the eventual outcome is that the number of the chosen item is returned to the main program for subsequent processing as the value of KWORD. However, several additional control facilities are provided within the software design in terms of 'master' commands which are available on most displayed frames at all levels. These commands will alter the control variables in various ways which will now be described.

SUBROUTINE MENU

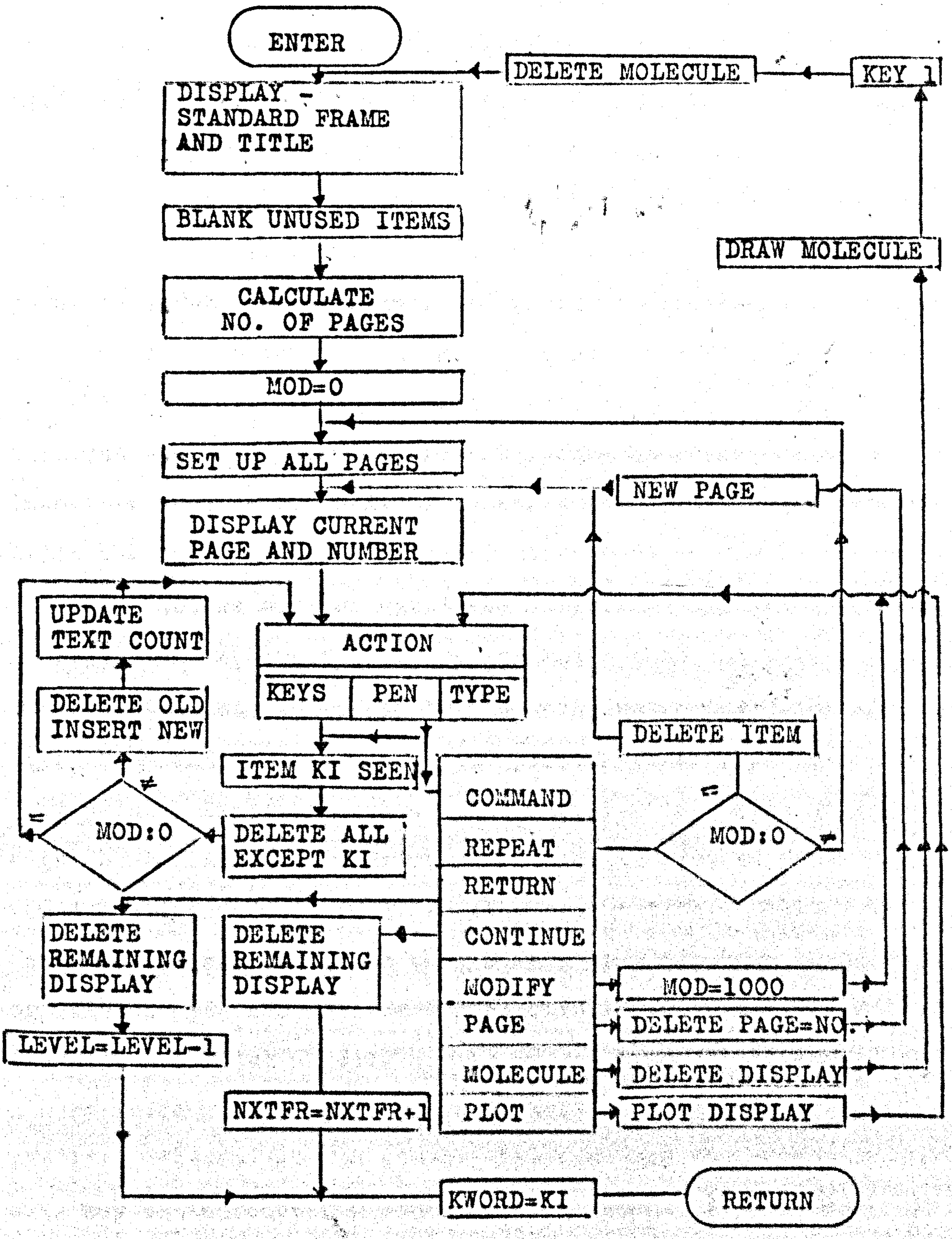


Fig. 3.4

The master commands REPEAT, RETURN, CONTINUE, MODIFY and PAGE appear in command 'areas' at the foot of the standard display frame (see figure 3.3) and are brought into operation by pointing the light pen at the appropriate command area and activating it using the foot switch. As such they assume control of the processing at this point of application. Alternatively the command may be typed in at the console keyboard. This mode of entry would be more convenient following an input of other information, textual or numerical, at the keyboard. The control functions of the master commands are described below.

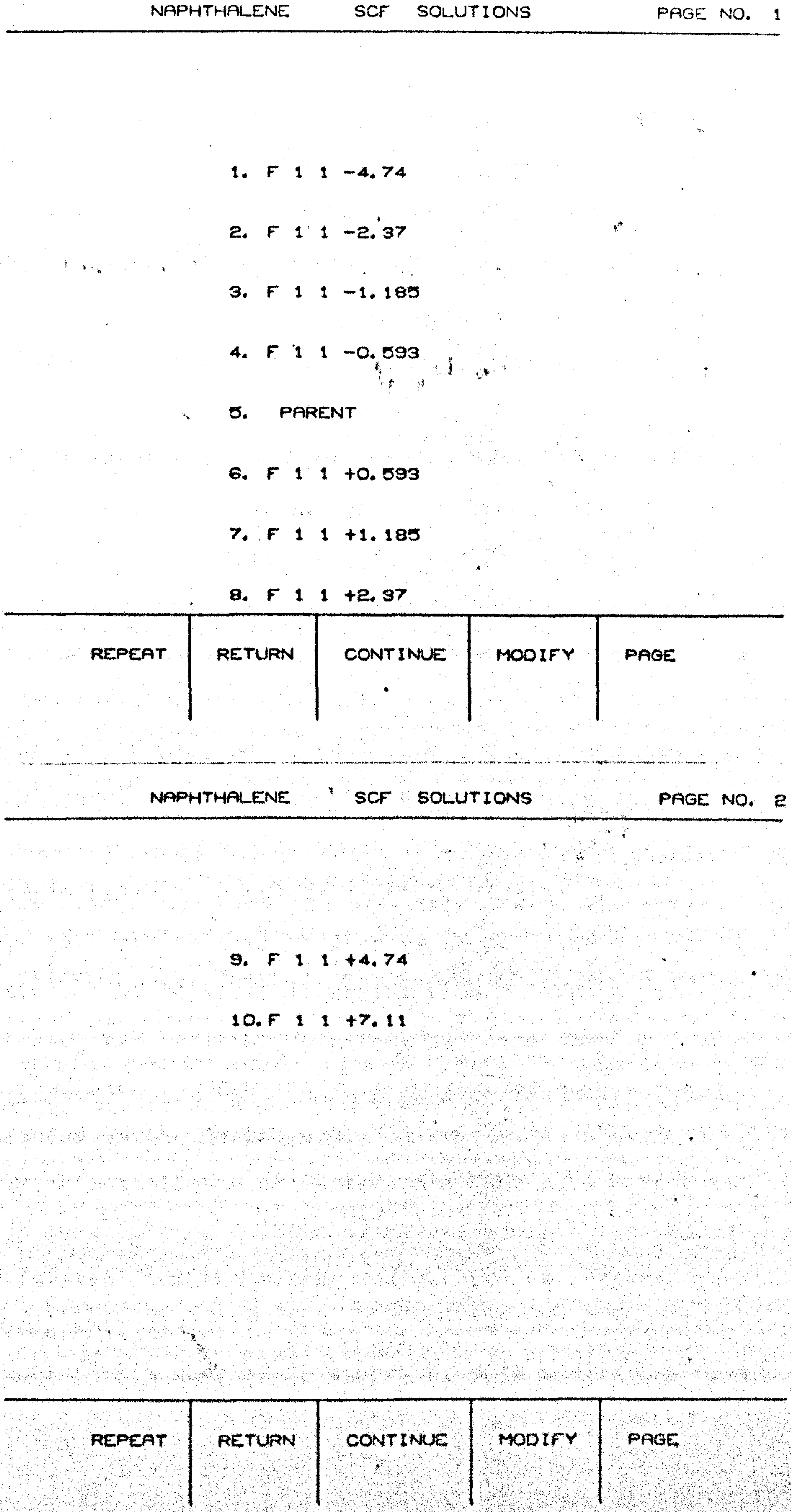
REPEAT re-writes the current menu. Its main use may occur when the user realises that he has chosen an incorrect menu item. In this case REPEAT will cancel the first choice and re-write the menu, enabling a second attempt to be made. Should the error not be noticed until the next frame appears (or even later), backtracking facilities are built into the system enabling the user to return to the point where the error was first made and to re-commence the program routing process from that point. Experience shows that REPEAT often saves what might be a considerable delay in recovering from an error which could initiate a relatively lengthy computation. Another use for this command may arise when a menu item has been added to or deleted from the list or modified for some reason. For example, a new set of data may be stored temporarily and given a name which will be typed in and added as a new menu item to the list of data sets in store. The name and the corresponding data may be subsequently modified or deleted. After these operations REPEAT can be used to re-write a menu and thus check that the alterations have been correctly made. REPEAT may be used as often as necessary at any decision point in the program where it appears in the standard frame.

RETURN is the command which initiates the backtracking process mentioned previously. Selection of RETURN transfers control back to the beginning of the current level of the main program. The user may at this point wish to re-commence the phase of activity, subsequently taking the same route as before or possibly taking a different option. Alternatively a jump back to the beginning of the previous level may be accomplished by selecting RETURN yet again. This speedy backtracking process is facilitated by the RETURN command always appearing at the same position on the display screen. Once the light pen is held in position against RETURN on the screen, it simply requires a sequence of foot switch activations to produce backtracking through the levels of the main program-to the beginning if need be.

CONTINUE is used mainly by way of confirmation that a menu item has been correctly selected and is acceptable. Selection of an item may be made by depressing the correspondingly numbered display console key or by pointing the light pen at the actual line of text constituting the menu item. This is possible because each menu item is entered into the display as a separate display item and as such has a number or numeric key, KWORD, and can be 'recognised' by the light pen. When a selection has been made, MENU automatically deletes the remaining items from the screen. If the single item now displayed is acceptable the user chooses to CONTINUE along the selected branch to the next frame. Alternatively he may use REPEAT and re-select in the manner already described. If no selection is to be made from the current menu, CONTINUE may still be used since NXTFR is automatically incremented by one and KWORD is set to zero when CONTINUE is used without an item having been selected. This procedure therefore promotes a transfer to the next frame in the sequence of numbered frames at this level.

MODIFY is used to indicate that the next menu item to be selected is due to be modified or re-written in some way. This is most likely to be used when some computed data set or curve or a new solution is to be given a name which could be saved only for the duration of the current application or which is intended to become part of the permanent text of a menu. The menu item chosen for modification will usually be a blank space on the screen initially, to be supplied with a new name typed in by the user within the MODIFY section of MENU. The appropriate piece of information which is to be stored will be buffered in the order corresponding to the list of given names and may be recalled from store later by the normal MENU selection procedure. This ordered storage of information is achieved by MENU returning a value in the argument variable MOD to the main program to be used as an indication of which of a set of storage vectors is to be used for the new piece of information. MOD is set to zero if no menu item modification has been made within MENU. If the menu refers to buffer-stored vectors, for instance, and, on leaving MENU, MOD is zero but KWORD is non-zero, this indicates that the vector corresponding to KWORD is to be recalled from the set of storage vectors to be used for either display or processing. Since MODIFY is used relatively infrequently it was considered desirable to present to the user, at the appropriate execution time for the command, a special message display consisting of instructions which identify steps to be followed in the procedure. These are analogous to the more elementary forms of explanation discussed earlier and are considered to be necessary within the MODIFY procedure. As mentioned earlier, it is recommended that REPEAT be requested to check that the modification has been written up correctly within the array WORDS.

PAGE is the last of the master commands which are available. The number of items required in a menu list at a particular level may, in practice, exceed the number which is convenient to display on the screen at any one time. Currently a maximum of eight items of the menu can be simultaneously displayed. This number was chosen objectively because it gives a simple correspondence between the items and the eight keys of the display console. It also gives a readable menu without presenting too much information to the user in a single display. This permits easy decision making which is relatively free of errors and user frustrations. Eight lines of text in the space provided give a pleasing appearance and are unambiguously picked up by the light pen if desired. To overcome the problem presented by a menu of more than eight items, MENU has a paging facility. This divides menu texts into pages of eight items which can be 'flipped' using the PAGE command. The page number at the top of the frame and the item counting and enumeration conventions keep track of the paging throughout. On reaching the last page of a set, a further request of PAGE takes the user back cyclically to the first page again, and so on. An example of a pair of pages is



NAPHTHALENE SCF SOLUTIONS PAGE NO. 1

1. F 1 1 -4.74

2. F 1 1 -2.37

3. F 1 1 -1.185

4. F 1 1 -0.593

5. PARENT

6. F 1 1 +0.593

7. F 1 1 +1.185

8. F 1 1 +2.37

NAPHTHALENE SCF SOLUTIONS PAGE NO. 2

9. F 1 1 +4.74

10. F 1 1 +7.11

Fig. 3.5

shown in figure 3.5.

Two further global or master commands are available within MENU. Since these are used much less frequently than those described above they are not displayed in the control function area of the standard frame and hence are not accessible using the light pen. They must be typed in when required.

By typing MOLECULE whenever a menu is displayed on the screen, the current menu is deleted and is replaced by a geometrical representation, complete with numbered atoms, of the molecule at present under investigation. This facility is particularly useful when it is desired to check on the atom numbering scheme in use before undertaking further calculations, especially those relating to modification of atom or bond parameters. In this case instructions are also given on how to effect a return to the point in the program at which the reference to the molecule was requested. The previously deleted menu is re-written and the process commences once again.

The second of these commands is PLOT. Typing this command causes the whole of the current display to be drawn out on the graph plotter. The facility is useful when a 'hard copy' is required. When the plotting operation has been completed, control is passed back to MENU and display-controlled processing is re-commenced in the normal way.

Finally, after all the actions within MENU have been completed, any remaining menu items or messages and the standard frame are deleted from the screen and control is returned to the main program.

In practice this mode of interaction, with a dialogue based on MENU, proves to be comfortable to use and is 'safe' in the sense that user errors are rarely made and yet are in principle recoverable. It is ergonomically sound because the majority of operations are carried out with the keys and the light pen, which can be conveniently used by the left and right hands respectively, whilst simultaneously viewing the screen; the pen-activating foot switch is also easily accessible. A transfer of attention to the keyboard is made less frequently, and since this usually initiates some utility operation such as a plot or a data entry, it is not necessary to view the screen at this time. Thus a good continuity of operation is maintained.

MENU can be extended both by the interactive addition (and deletion) of menu items, and by the creation of further menus as the system develops, and as lists of options at new decision points are needed. Such extensions simply call for the appropriate allocation of space for the new menu on backing store and the organisation of program calls to the subroutine MENU in the main program, with a linked branching procedure for use on exit from MENU. The full range of facilities available in MENU may then be applied to the newly created list of options. This procedure for extending the MENU system proves to be very economical in terms of core space, since only enough core for a single menu needs to be allocated within the main program. Full details of the procedures used for storing and retrieving of menu lists from the menu file held in backing store will be given in section 3.6.

The menu mode of dialogue can be associated with and benefits from division of the main program into distinct phases or levels. As indicated earlier, most projects in quantum chemistry research which use a computer also fall into distinct and well defined processing parts. Consequently the present program is designed as a precise functional structure of levels and sub-levels, as given in figure 3.6, which reflects the distinctive pattern set by the problem solving approach taken when applying the semi-empirical approximation methods of quantum chemistry research.

3.1.3 Operating the System

(i) In the first step which is associated with the first level of processing, a particular molecule is identified for study. This is achieved by the user making a selection from a list of options presented in the opening frame appearing on the display screen. At this point a branch may be made either to one of the automatic 'molecule generating' routines or to a library list of molecules for which certain models and solutions exist already and are available on backing store. A third branch is to a section where information needed to define a molecule and to initiate a set of calculations is to be read from cards.

(ii) The purpose of the second level is to identify the type of molecular model which is to be analysed and to initiate the derivation of a solution from this model corresponding to the molecule specified in level one. The models can range from the simple Huckel type through various SCF-CI models. The choice of model can, in principle, be extended further, since the system is open-ended in this respect. Depending upon the

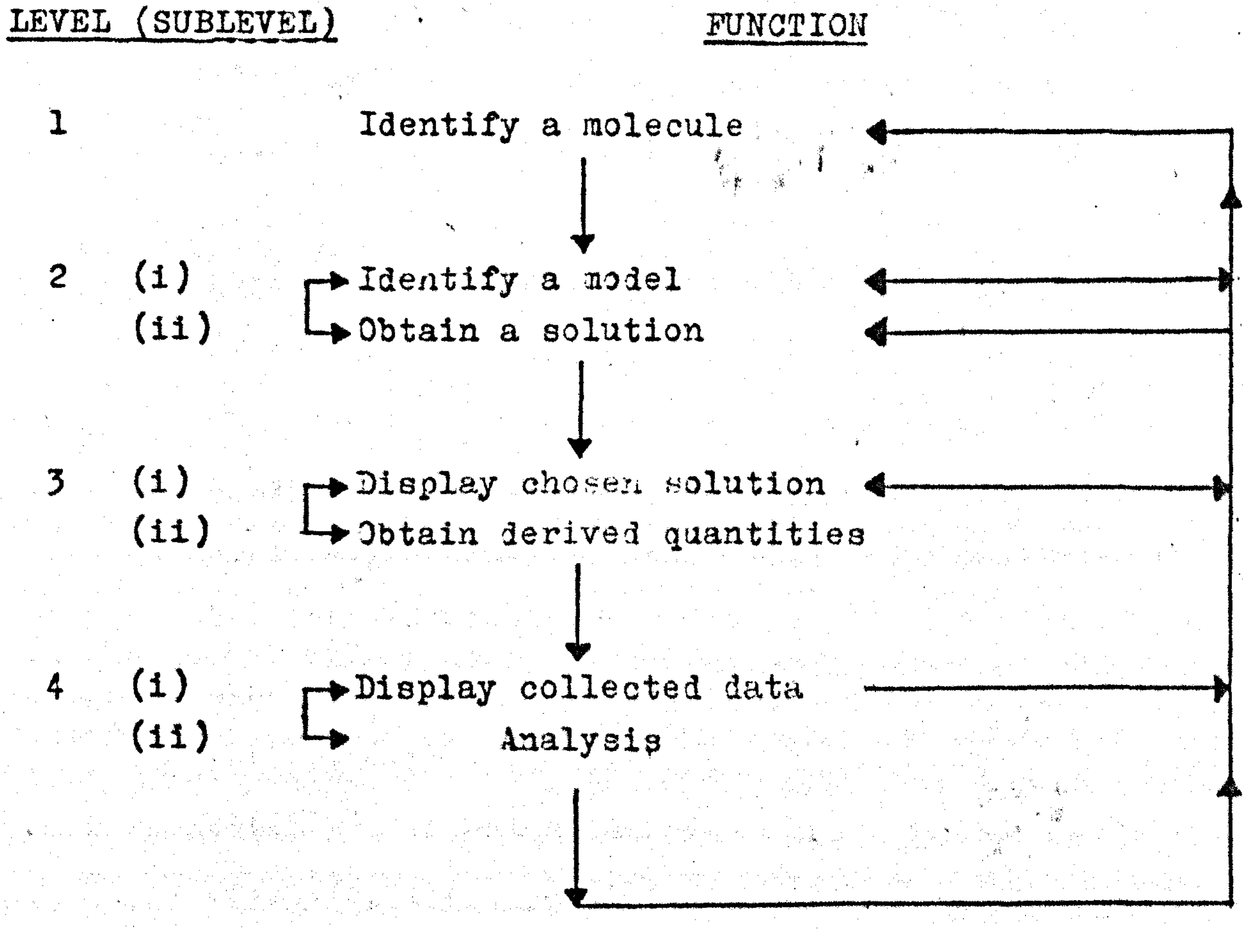

LEVEL (SUBLEVEL)
FUNCTION
1
Identify a molecule
2 (i)
Identify a model
(ii)
Obtain a solution
3 (i)
Display chosen solution
(ii)
Obtain derived quantities
4 (i)
Display collected data
(ii)
Analysis

Fig. 3.6

route taken as a result of the choice made in level one, solutions are obtained directly as a result of computations or as extractions from the library of solutions. In the former case the user is presented with the opportunity to specify parameter values interactively before the calculations are initiated. In the latter case selection may be made from a display summarising existing solutions, each specified by associated parameters. Discussion has already taken place on the extent to which solutions need to be stored and this question of storage will receive further attention in a later section. The amount of detail in a solution will vary depending upon the approximation method used but, fundamentally, a solution may be thought of as consisting of the set of ground state energy levels, the corresponding molecular orbitals expressed as LCAO coefficients and a parameter list indicating the number of atoms, their positions, the model type and other parameters as required by the model. For instance, each SCF solution has a parameter which indicates whether or not any associated CI solutions are available on backing store. Any such CI solutions can be located by the program and displayed or used for further analysis at the user's request.

(iii) The third level of the main program is entered as soon as the solution has been obtained. The first event to take place in this section of the program is the display of the selected solution. It may be examined in its parametric form or in pictorial representations of energy levels and molecular orbitals. On the basis of this inspection a choice may be made as to which properties of the solution or collected set of solutions are to be analysed. A menu consisting of a list of derivable quantities is automatically presented to the user. Results from the selected computations are temporarily buffered in core before an option chosen by the user indicates that the collection of data is now complete and is to be passed to level four for display and analysis.

(iv) Level four contains facilities for displaying and manipulating data, including such operations as deleting data points, creating image points and facilities for performing transformations and for fitting curves. Storage areas are available for retaining data sets and computed curves so that simultaneous displays may be made for the purpose of comparing two or more sets of results.

The permitted 'vertical' movements through the scheme of processing levels as indicated in figure 3.6 and the various possible 'horizontal' movements resulting from menu items selected within levels give rise to a vast number of potential 'routes' through the system. Considered in this way the system has the structure of a decision tree. The remaining sections of this chapter describe in some detail the branching possibilities open to the user as a result of decisions taken within each level. Because of the large number of possible outcomes, the descriptions and the related diagrams will generally refer to the routes typically taken in analyses using SCF-CI approximation methods.

3.2 The Initialisation Phase

The two main purposes of the first level of the main program are

(i) to identify a molecule selected for study and

(ii) to organise the permanent storage of results arrived at during the course of the program, when such storage is required.

Figure 3.7 is a flow diagram of level one, showing possible 'routes' of the kind used in the applications described in later chapters.

When the main program is loaded, the initial display frame, which may be thought of as the 'keystone' of the program or the 'top' of the decision tree, appears automatically. This frame lists all the molecule selection options to which the program may branch. It also acts as the point at which a decision to exit from the program or to store results permanently may be made.

A molecule may be selected in any one of three different ways. It is possible to select special molecule generating routines which enable the user to nominate a particular member of a family of molecules. Two such routines are used in the applications to be described in subsequent chapters. One of these generates the planar hexagonal grid scheme for parent hydrocarbons which is described by Greenwood (1). A call to subroutine SELMOL is activated by the selection of the first menu

LEVEL 1

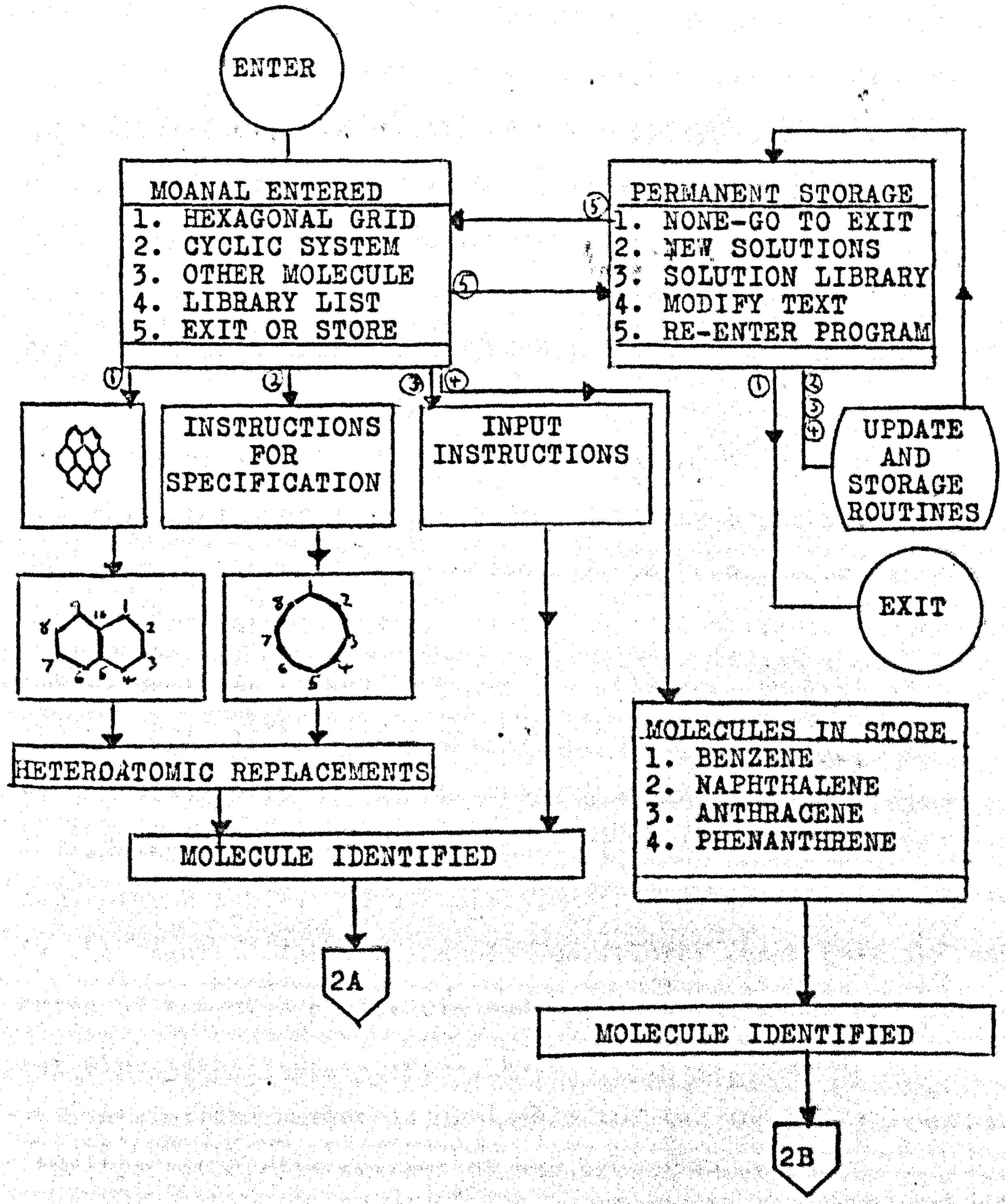


Fig. 3.7

item in the initial display. The entire hexagonal grid then appears on the screen in place of the decision frame. Figure 3.8 is a reproduction of the actual display at this time. A tracking cross which follows the light pen whenever the latter is activated is also visible in the display. The user now directs the cross to individually selected atomic positions, indicating when each selection has been made by depressing the first of the display console keys. When the complete molecule has been thus described, key number two is depressed and this results in a fresh display of the chosen molecule, with the atoms numbered in the order selected, shown independently of the rest of the grid. Figure 3.9 shows the naphthalene molecule derived in this way. A facility is incorporated in the program for interactively making single or multiple heteroatomic replacements of carbon atoms at this stage. The user re-traces the molecule in the order given by the numbered atoms and at each atomic position the replacement is made by selecting a key corresponding to the replacement N or O etc., as indicated in a displayed table. If no selection is made a default to carbon is the result. The routine also calculates the atomic co-ordinates of the chosen molecule and supplies these and code for the atom identities to level two of the main program.

A similar routine is available for the specification and depiction of cyclic systems of any prescribed order.

Whenever such a procedure has been used to define a molecule, the final 'picture' is retained throughout the computation and may be referenced at any time as was described in section 3.1.2.

If it is desired to study the properties of a molecule for

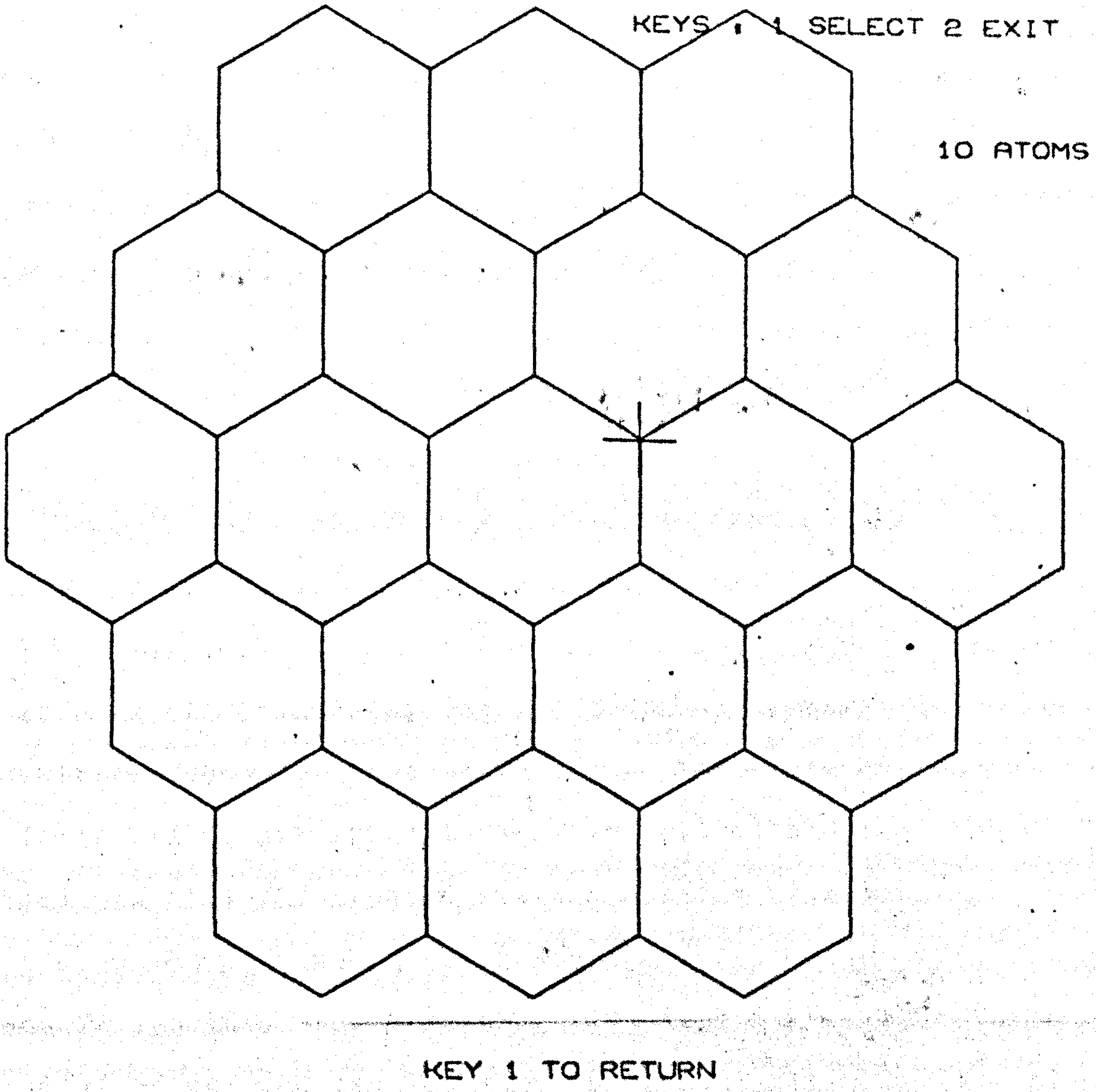


Fig. 3.8

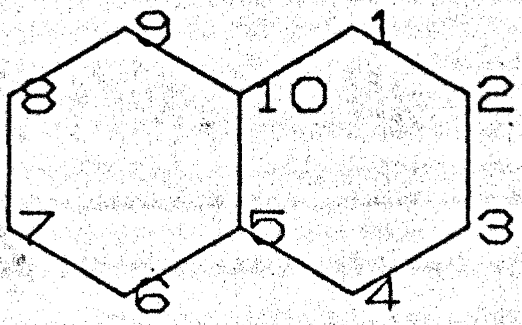


Fig. 3.9

which there is no 'generator' available, then the information which the routines would normally supply may be input on cards. Suitable provision of the appropriate cards must be made and they must be presented in accordance with displayed instructions. Naturally, in order to preserve the interactive mode of operation, any such cards should be prepared before running the program. The selection of menu item number three in the first frame initiates this alternative procedure.

Each of the above courses of action implies that a new solution or set of solutions is about to be computed. However, it will be realised that sets of solutions have many properties and it is possible to derive, for the purposes of analysis, several quantities from the solutions. It may therefore not be possible or desirable to attempt all the computations and analyses at one 'sitting'. For this reason and to minimize time spent re-computing solutions, a comprehensive storage facility for sets of solutions is provided. By selecting menu item number four the user obtains a displayed list of those molecules for which solutions are currently held on backing store. In turn, a selection from this 'menu' identifies the chosen molecule in readiness for entry into level two.

Thus the second level may be entered in two different ways - via the 'new solution' route or via the 'library solution' route.

The other function of level number one is that of initiating and organising the permanent storage of solutions and display information. In general it will be found desirable to make permanent storage arrangements immediately prior to an exit from the program. Hence the exit and permanent storage operations come close together in the logic of the program and the path leading to both is opened by the selection of item five in the first frame of level one. This is the only valid exit route, although exits may be (rarely) caused by unforseen user activated run-time errors. Consequently, upon completion of work at any level the user must back-track in the manner indicated in section 3.1.2 to the initial frame. This necessity and that for a further conscious selection in the 'permanent storage' frame are safe-guards against accidental exits or erasures.

On reaching the permanent storage section of the program the procedure is as follows. If a new solution or set of solutions has been created and permanent storage is desired, it may be achieved by selecting menu item number two in the displayed list of options as shown in figure 3.7. The effect is to allocate a new area of backing store and to correspondingly update the directory of solutions.

If work has been under way with a solution or group of solutions originally abstracted from the library and modifications to the solutions have taken place in core e.g. one of the set of library solutions has been replaced by a newly computed solution, then the current core version of the set may be transferred to the library in place of the original by the selection of the third option in the displayed frame.

The fourth option at this stage permits permanent modifications, additions and deletions to be made interactively to the texts in the menu frames. In practice only a few of the menu texts are subjected to frequent alteration in this way. It is those frames in which the menu items are names used to refer to currently stored data sets or curves which receive most attention. Others changed less frequently include those representing lists of solutions in permanent store or sets of analytical or branching procedures which are updated only occasionally. However, in the early development stages of the program, changes of this type naturally occurred more frequently. It was found to be advantageous at that time to maintain all the texts on cards and to read them into core every time the program was run. The price paid in terms of core space used and card reading time was offset by the availability of a visible set of text records which could be modified off-line to keep pace with program development. As the size of the program and the number of texts grew, core space was at a premium and the read-in time began to be tediously lengthy. Hence the current version of the program uses a different arrangement whereby all the frames are regarded as permanent and they are retrieved individually, by subroutine FWRDS, from backing store for use within the MENU subroutine. Consequently any modifications made to a frame inside MENU, during the course of the program run, are also regarded as permanent unless subsequently cancelled before an exit is finally made. A special routine to deal with this is incorporated in the fourth option at this stage. All frames to which modifications have been made are displayed one by one on the screen. The user then requests MODIFY, followed by a menu item indication. The item is then 'deleted' by blanking off the text both in core and in backing store. Thus it is possible to 'clean' a whole menu or part of a menu, item by item. The facility is particularly useful when a re-entry to the program is desired with only parts of certain frames remaining intact.

Further details of methods adopted to effect transfers to and from backing store and of modes of storage will be given in section 3.6.

3.3 Obtaining a Solution

As indicated in the previous section, the second level of the main program may be entered along two different routes, namely the 'new solution' route or the 'library solution' route. In both instances, with a molecule having already been identified, the first frame presents to the user the range of models which are available, together with their corresponding solution procedures.

When a new solution is required to be computed, a check is first made in order to verify that the routines can accommodate the proposed molecule. There is a limit to the size of molecule each set of solution procedures can deal with, owing to demands on core space. In addition, the number of integrals etc., available on file must necessarily be limited. A warning appears on the display screen if the selected molecule and model are incompatible at the time of the proposed experiment. If all is well, however, a message indicating any special data requirements relating to the selected model appears instead.

A flow diagram of the routes through level two for the Pariser-Parr-Pople SCF-CI procedures, with several permitted variations, is given in figure 3.10. As may be seen from the diagram, the user is first given the opportunity to choose how the basic parameters (i) the two centre electronic repulsion integrals, $\gamma_{\mu\nu}$ and (ii) the resonance integrals, $\beta_{\mu\nu}$ are to be

LEVEL 2

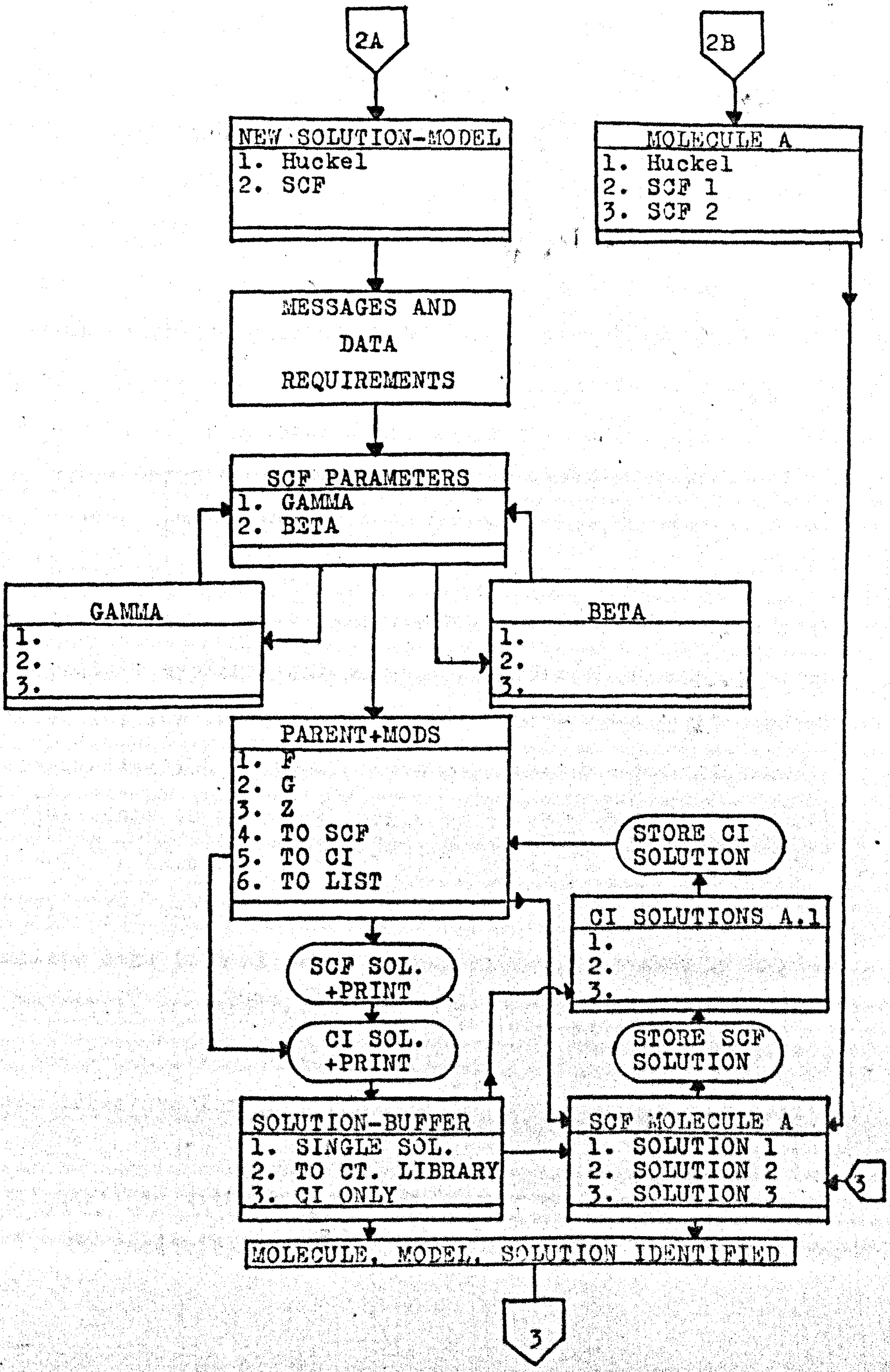


Fig. 3.10

defined and computed. The selection is made by indicating in turn one of the named procedures in the 'GAMMA' and 'BETA' menus. This results in the appropriate subroutines being used henceforth in the experiment until such alternatives that may be desired are specified. The one-centre integrals $\gamma_{\mu\mu}$ and several other parameters needed by the methods for determining $\gamma_{\mu\nu}$ and $\beta_{\mu\nu}$ are stored on permanent file. If no selection is made at this stage, the program defaults to Pariser and Parr's parameter specifications,{7,8}. Actual methods which have been used with the system and some experimental results obtained will be described in chapter four, along with details of the SCF-CI routines which have been modified for interactive use.

Although $\gamma_{\mu\nu}$ and $\beta_{\mu\nu}$ can be set automatically, even for heteromolecules specified interactively in level one, it is still desirable to have the facility for making further modifications to real or hypothetical parents in order to derive additional molecules for investigation. So, before commencing the SCF diagonalisation section, it is possible to make individual adjustments to matrix elements of F (core matrix), G (electron repulsion integrals matrix) or Z (effective nuclear charge vector). The modifications are made by first indicating the appropriate menu item as shown in figure 3.10 and then by typing in the matrix row and column references followed by the actual value to be given to the nominated element. These modifications are effective for the current solution only, but the original parent molecule core matrix may be recovered intact for further calculations without the necessity of re-constructing it.

On receiving the indication that modifications have terminated, the program proceeds to the SCF routines, ending the iterative process when self consistency has been attained to within a prescribed tolerance. The results are printed out to give a permanent record. If a CI solution has also been requested, the user specifies the replacement configurations and this computation then takes place, to be followed by a further printout.

Display and analysis of both the SCF and the CI solutions thus obtained may now be undertaken. The user selects the first of the routes indicated in the next frame and the program proceeds to level three. Alternatively the SCF solution (energies, molecular orbitals, parent details and modifications) may be stored in the current solution library. For smaller molecules current solutions are kept in core, but for larger molecules backing store is used. Which of these storage modes is actually to be used is determined within the program on the basis of molecule size. At this point in the program the user should up-date that menu which lists the named solutions in their order of storage. Each SCF solution thus stored may have several CI solutions associated with it. For instance, solutions may be stored for a given range of F(I,I) values (I fixed), each of these SCF solutions having associated CI solutions over a range of G(I,I) values. Stored solutions of this type will be used in the discussion and analysis to be presented in chapter five. In actuality only a reduced version of the complete CI solution is stored. This consists of a note of the modifications and replacements along with the resultant intensities and state energies. It is difficult and rarely worthwhile to store more than this, even for relatively small molecules. The state wave functions for instance are particularly bulky and, with several CI solutions for each SCF solution the complete storage of all the solutions ceases to be a practical proposition.

The program now loops back so that another modification of the same parent may be made for a further complete or partial SCF-CI computation. Alternatively a back-track may be made in order to bring in new $\gamma_{\mu\nu}$, and/or $\beta_{\mu\nu}$ specifications or, going further up the tree, a new parent molecule may now be introduced for comparison. Solutions from any source may, therefore, be buffered before proceeding to the display and derived quantities section - either with individual solutions from the newly created set or, as is more convenient for some purposes, with the entire solution set. To take the entire set forward no individual item is selected from the displayed list of solutions. Instead, the user simply requests CONTINUE. The display part of the next section is by-passed and, whatever the quantity required (bond order, charge density etc.) it will automatically be evaluated for all solutions in the set.

A similar list of library solutions is displayed when, after the model type has been identified, entry is made to level two via the library solution route. Once again the selected set of solutions will be held in core for smaller molecules or in backing store for larger ones and individual large solutions or the whole set of smaller solutions may be similarly taken to the following level of the program. It is possible to replace a library solution by a newly computed solution. With the original (set) established in core, the replacement solution, arrived at by a back-track up the tree, followed by a return down the new solution route, will be added to the core version in the specified position, when the corresponding menu is amended by the user. The modified library set may then be made permanent on exit from the program via the normal route in level one. Several solutions in a set may be replaced in this way.

The hierarchical scheme for classification of solutions, consisting of numbered molecules, approximate methods or models and individual solutions is indicated by the reference number, NSOL, given to each solution. This number enables any single solution to be accessed from the library and, by its nature, makes a solution readily identifiable when the number and the solution details are displayed together. NSOL is defined -

NSOL = 1000*KMOLS + 100*MTYPE + KSOL

where

KMOLS is the molecule directory reference number,

MTYPE is the model identifier (=1 for Huckel, = 2 for P-P-P SCF, etc)

KSOL is the solution number in the specified set and will be identified with specific parameter values.

3.4 Derived Quantities

In level three the chosen solution may be displayed for examination in a variety of ways before it is used within the level for the derivation of such quantities of interest as bond orders, charge densities, dipole moments or oscillator strengths.

A flow diagram of level three is given in figure 3.11.

LEVEL 3

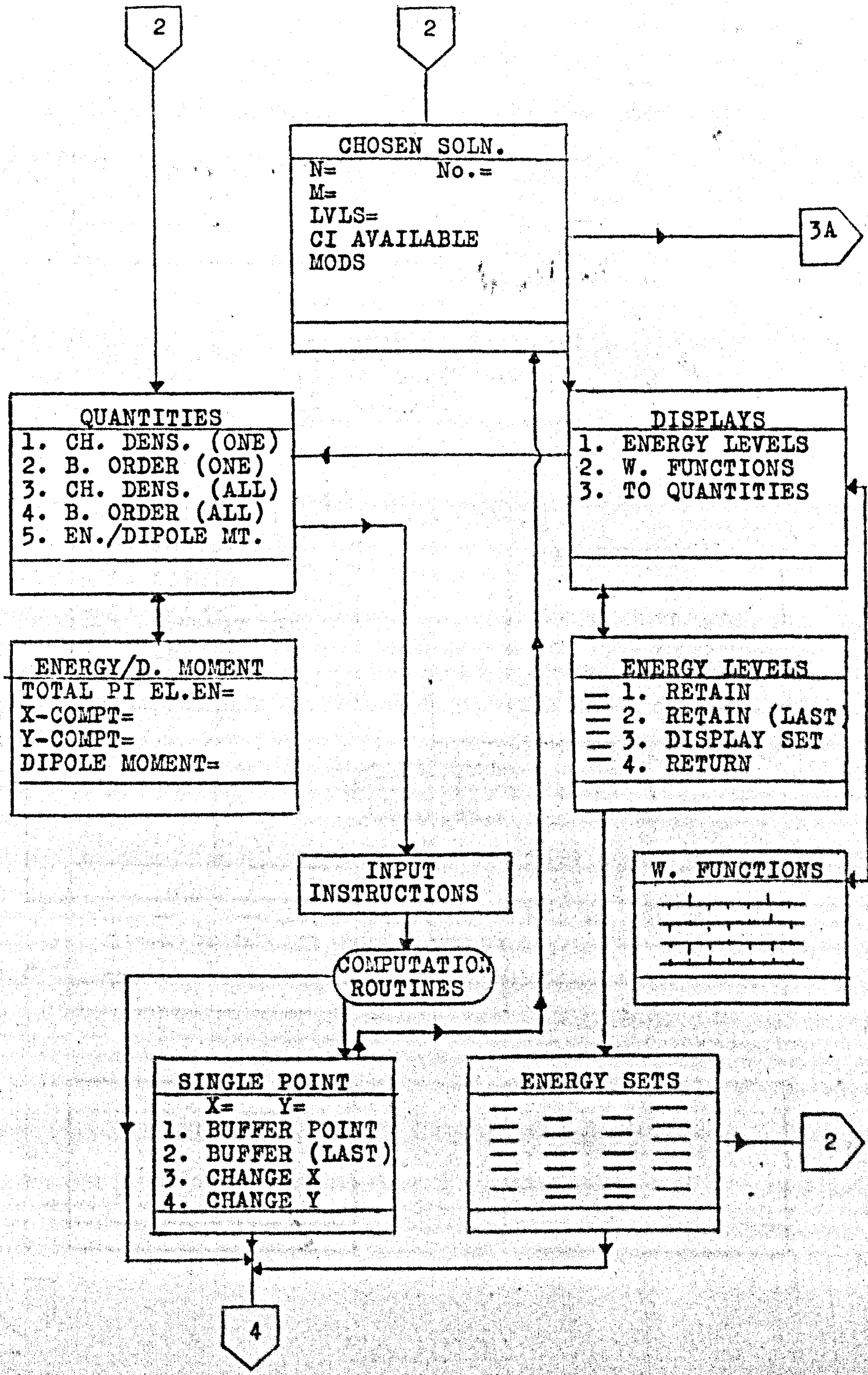


Fig. 3.11(a)

LEVEL 3

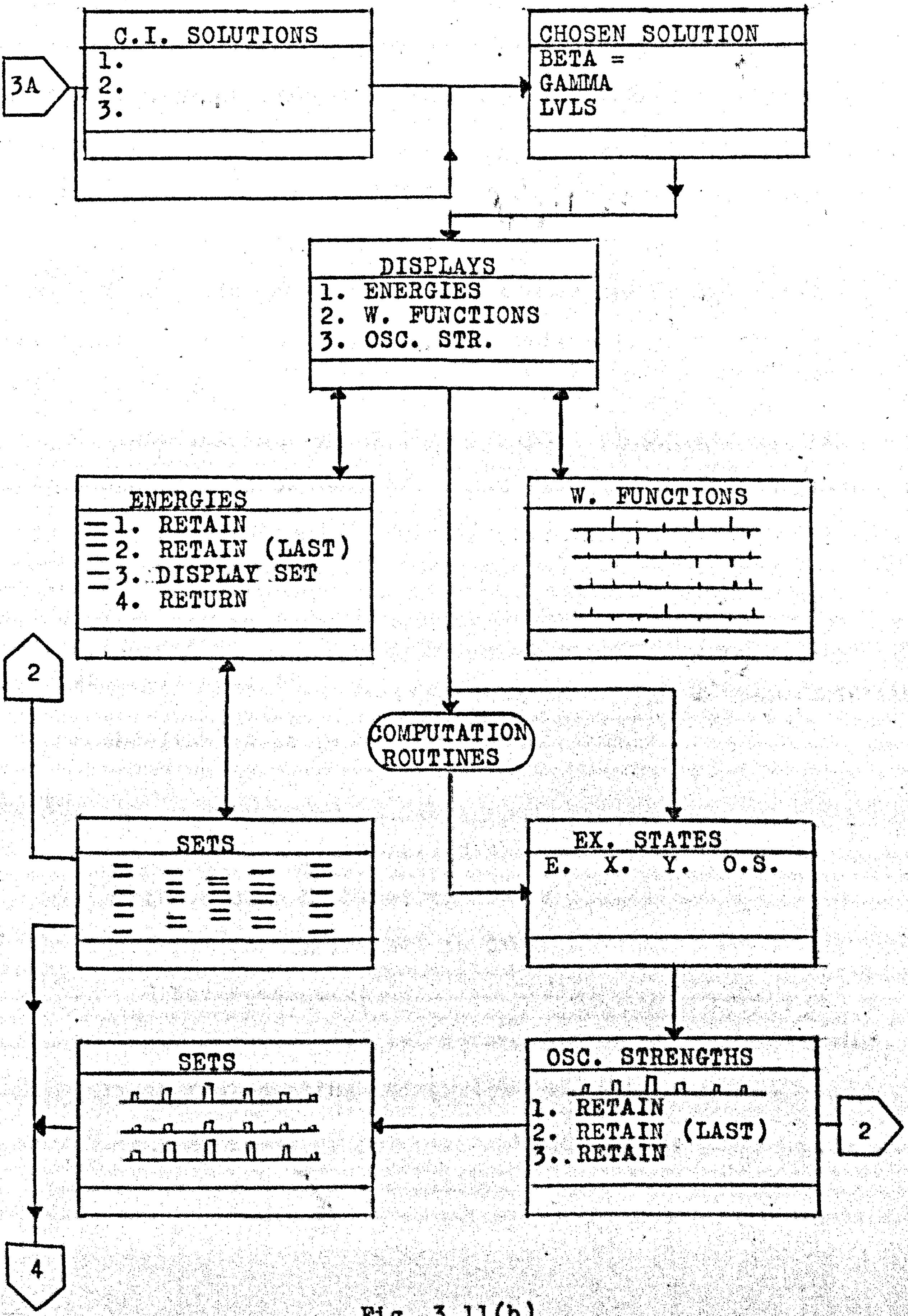


Fig. 3.11(b)

A parametric summary of the individually selected solution is displayed immediately on entry to level three. An example of this display for a derivative of the naphthalene molecule in a Parr-Pariser-Pople formulation is shown in figure 3.12. It will be seen that this solution refers to a modification in F(1,1) of -4.74 (i.e. 2 x $\beta_{\mu\nu}$), that the individual solution reference number is 2201 (i.e. the first solution of the set of P-P-P solutions from the naphthalene parent) and that a CI solution exists and may be examined on selection of key number four. The source of the parent in terms of hexagonal grid 'atom' numbers is also given.

On reaching this point at any time both the set of energy levels and the set of molecular orbitals for the SCF solution itself may be displayed by selecting the appropriate menu item in the next frame.

The energy levels are displayed as shown in figure 3.13 by means of a call to

```
SUBROUTINE ENDIS (N,V,IT,X,XH,S,VI,NBUFF)
```

where

N is the number of energy levels

V is the vector of N energy levels

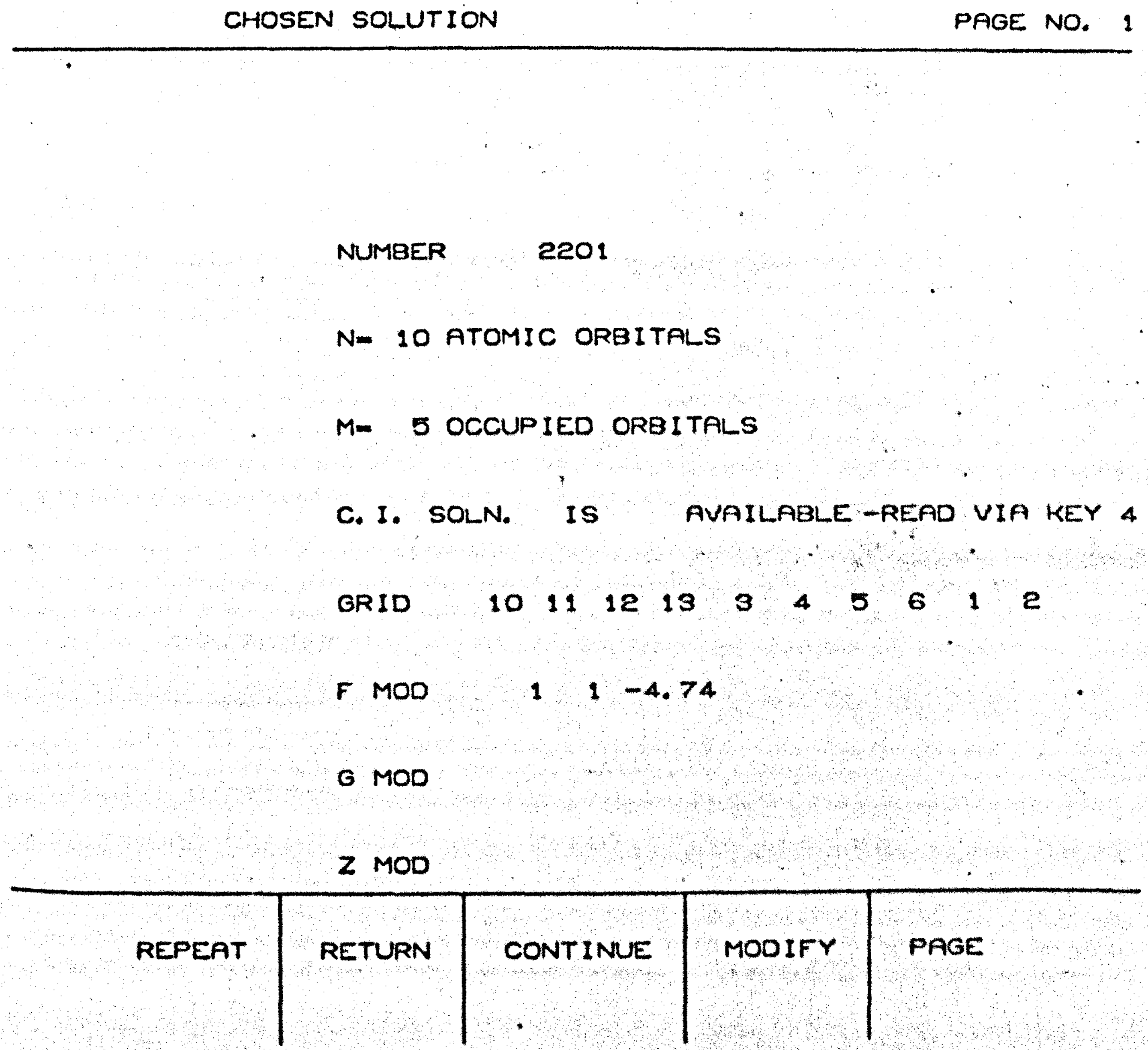
IT = 0 for the first call to ENDIS

0 for subsequent calls to ENDIS

X is the required initial x-co-ordinate of the horizontal lines representing energy levels

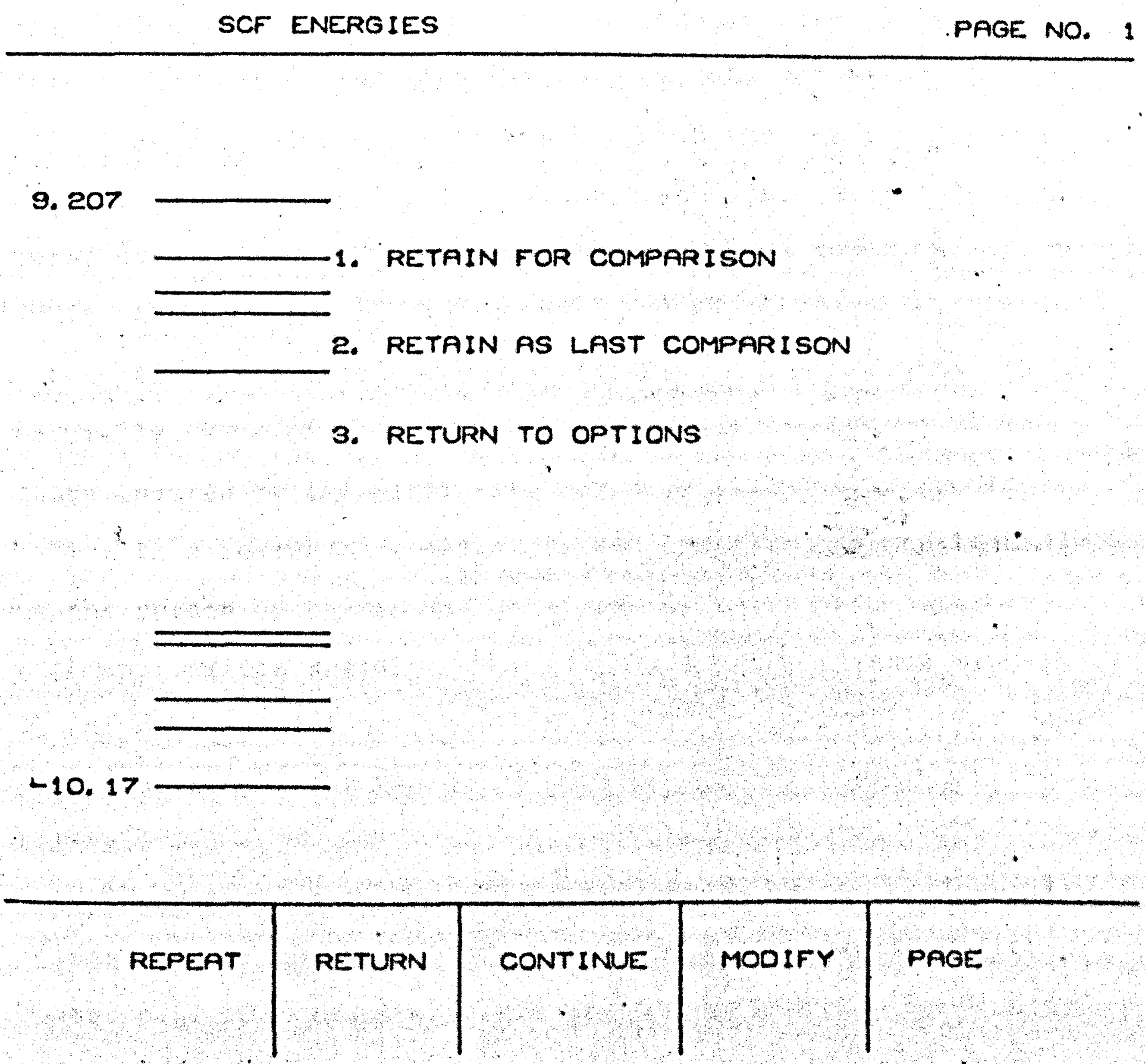
XH is the length of the lines beginning at X

S is the vertical scale factor



```
CHOSEN SOLUTION                                    PAGE NO. 1

          NUMBER     2201

          N= 10 ATOMIC ORBITALS

          M=  5 OCCUPIED ORBITALS

          C. I. SOLN.   IS     AVAILABLE -READ VIA KEY 4

          GRID    10 11 12 13  3  4  5  6  1  2

          F MOD     1  1 -4.74

          G MOD

          Z MOD

    REPEAT     RETURN     CONTINUE     MODIFY     PAGE
```

Fig. 3.12



SCF ENERGIES PAGE NO. 1

1. RETAIN FOR COMPARISON

2. RETAIN AS LAST COMPARISON

3. RETURN TO OPTIONS

Fig. 3.13

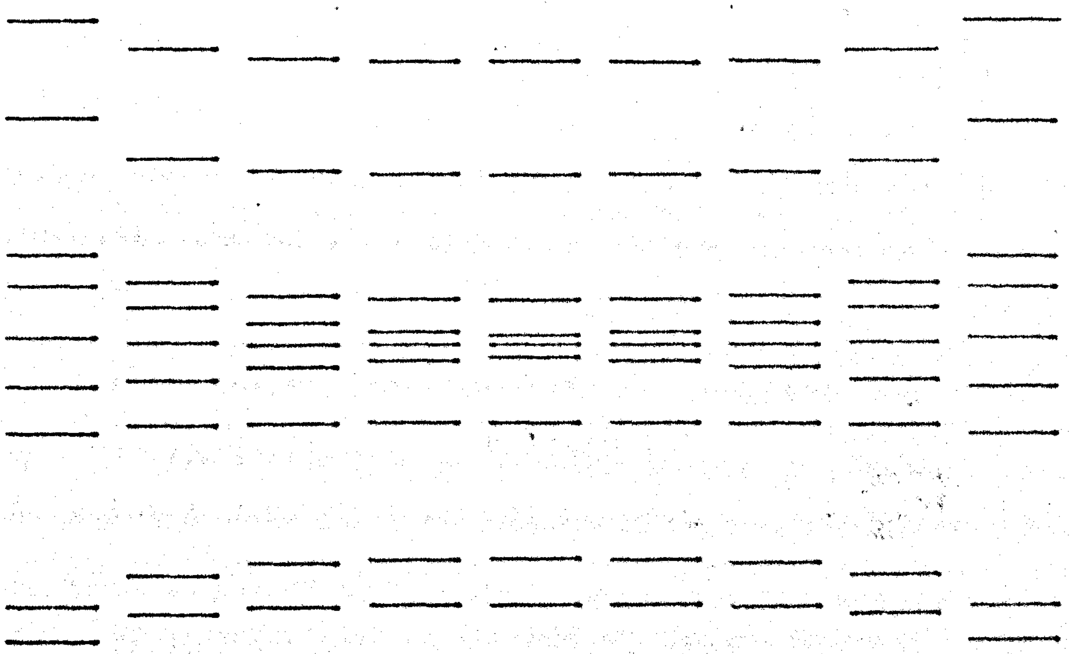
VI is the value of the lowest energy

NBUFF is the display code buffer

In the first call (IT = 0) the values of S and VI are determined from the values presented in V and are passed back to the main program to be used as reference values for subsequent calls to ENDIS. Alongside the lowest and highest levels, their numerical values are displayed. The subroutine takes account of degenerate levels, indicating an n-th order degeneracy by displaying (n) at the side of the line representing the degenerate level.

Energy level vectors may be buffered and later displayed for comparison as a complete set as shown in figure 3.14. In this case, each 'column' of levels is displayed in a separate call to ENDIS, the position of the lowest level of the first column and its vertical scale being used as references for the other columns. Naturally, some of these other energies may extend out of the range covered by the first set. This is allowed for automatically, to a reasonable extent, by the conservative positioning on the screen of the lowest level of the first set, together with appropriate scaling. For a block display of this kind the actual horizontal line length is scaled automatically, the value being based upon the number of vertical sets currently in the buffer.

The variation of any one of the energy levels horizontally across the set may be plotted by typing in the required level number; e.g. '01' results in all the lowest energies on display being collected into an array which is passed to level four, together with a second array containing the values of the independent variable associated with each vertical set of energies.



```
FOR PLOT TYPE IN NO. OF EN. LEVEL(12) OR 'OO' FOR NO PLOT
```

Fig. 3.14

ENDIS is also used for displaying sets of CI transition energies which may also be buffered as described above. An additional interactive facility can be extremely valuable at this stage. For plotting, the levels may be nominated individually by the user, taking one from each column, moving left to right across the screen. Since the levels are always arranged in ascending order of magnitude by the diagonalisation routines, there can be no indication from the energies alone as to which spectroscopic band a particular energy relates. Thus the automatic plotting procedure described above, although rapid, may in fact incorrectly take energies from different bands. However, if through examination of the wave functions and intensities, or otherwise, the user is aware of 'crossing' of energy levels, the true plot may still be obtained by selecting the points individually. If, on reaching the data display section an incorrect data point selection becomes evident, an immediate return to the energy diagram can be made and the selection procedure can be re-commenced.

This is an instance where interactive graphics is of considerable value in the analytical process. The standard pre-programmed package is unlikely to be able to deal, unaided, with this kind of situation, yet with knowledgeable and timely assistance from the user, the computer is able to produce the true and accurate picture required.

The wave functions in both the SCF and the new CI solutions are displayed by calls to

```
SUBROUTINE WFDIS (T,N,LL,LH,LIN,KK,NBUFF)
```

where

N is the number of wave function components

T is the array of wave functions

LL,LH are arrays indicating replacements

LIN = 0 for SCF displays

> 0 for CI displays (to include replacement information)

KK notes which wave functions are to be displayed

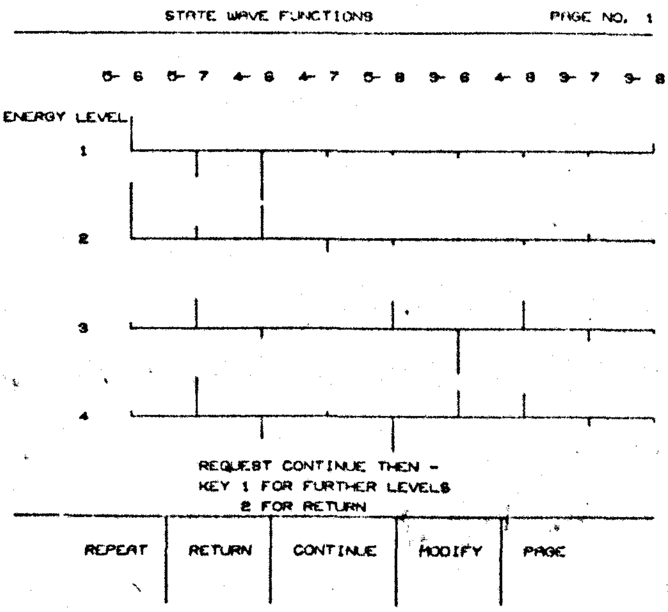
NBUFF is the display code buffer

The wave functions are diagrammatically displayed, four at a time, and each may be seen as often as desired by repeatedly 'flipping' the 'page', using the keys - as shown in figure 3.15. This figure shows how the nine state wave functions appear in the CI solution of a naphthalene derivative, using all possible single replacements but involving the six innermost ground state energy levels only.

WFDIS can show both SCF and CI solutions of any size in this way, giving the clearest possible rapid demonstration of the magnitudes and signs of the wave function components.

From the SCF solution, several quantities may be computed at the user's request. The charge density at any specific atom is computed on typing in the atom number. The value obtained is displayed and it may be buffered for later plotting, along with the corresponding value of an independent variable.

As points are collected in this manner they are displayed and may be adjusted in their x or y components or in both. Amongst other advantages this gives the user the opportunity to change the y-axis of the plot to, say, a variation in charge



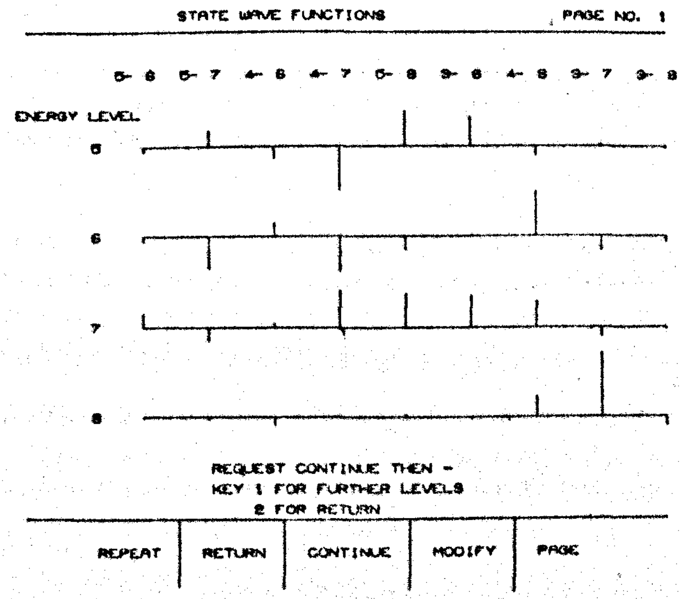
STATE WAVE FUNCTIONS PAGE NO. 1

5- 6 5- 7 4- 6 4- 7 5- 8 3- 6 4- 8 3- 7 3- 8

ENERGY LEVEL

REQUEST CONTINUE THEN -
KEY 1 FOR FURTHER LEVELS
2 FOR RETURN

REPEAT	RETURN	CONTINUE	MODIFY	PAGE



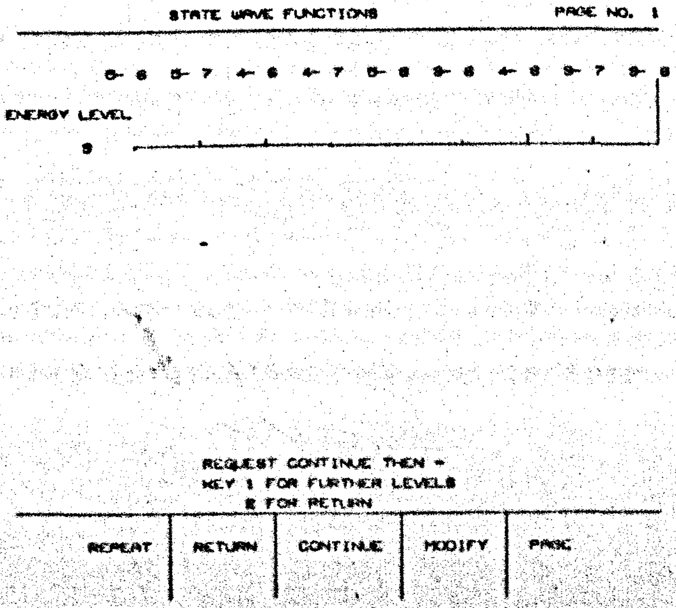
STATE WAVE FUNCTIONS PAGE NO. 1

5- 6 5- 7 4- 6 4- 7 5- 8 3- 6 4- 8 3- 7 3- 8

ENERGY LEVEL

REQUEST CONTINUE THEN -
KEY 1 FOR FURTHER LEVELS
2 FOR RETURN

REPEAT	RETURN	CONTINUE	MODIFY	PAGE



STATE WAVE FUNCTIONS PAGE NO. 1

5- 6 5- 7 4- 6 4- 7 5- 8 3- 6 4- 8 3- 7 3- 8

ENERGY LEVEL

REQUEST CONTINUE THEN -
KEY 1 FOR FURTHER LEVELS
2 FOR RETURN

REPEAT	RETURN	CONTINUE	MODIFY	PAGE

Fig. 3.15

density from some original value or to re-scale an axis, possibly into units of $\beta_{\mu\nu}$.

A similar procedure obtains for plotting bond orders, this requiring the input of the two atom numbers concerned.

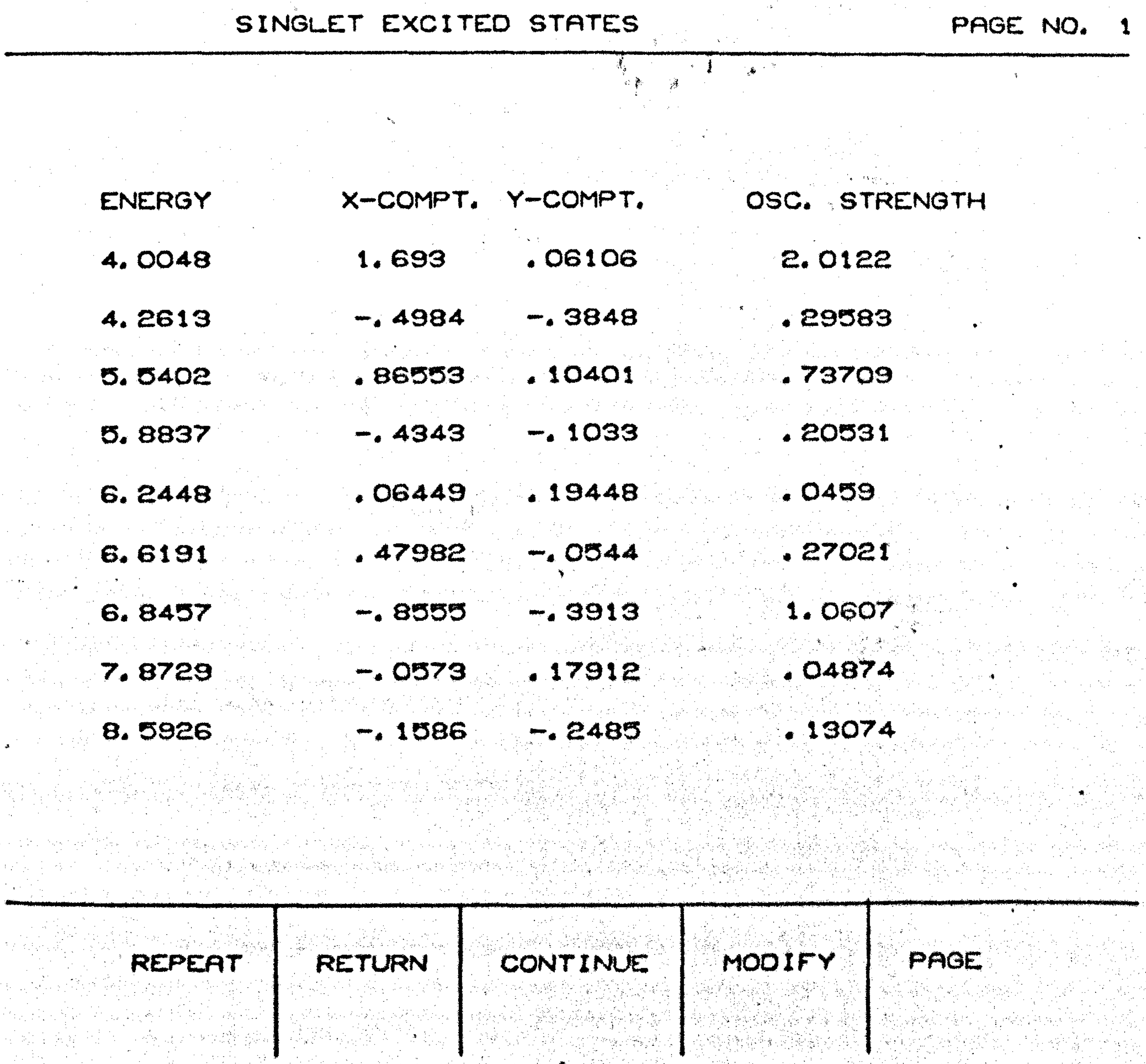
To save time when generating these arrays for a given set of solutions, the nominated quantity can be computed for the entire current set at the request of the user. Once computed, the arrays are buffered in readiness for a straight-forward plot of the quantity versus that modification which distinguishes the solution. If there are several such modifications the user must indicate which particular one is to be operative.

The values of the total pi-electron energy and the dipole moment and its components may also be observed, by request, at this stage.

The new CI solution may itself be processed to give component transition moments and oscillator strengths for transitions from the ground state to the excited states. These results will be displayed as shown in the example given in figure 3.16.

As noted earlier, the oscillator strengths and state energies are stored as part of the CI solution. A pictorial representation of energies and intensities, resembling the spectrum, from the new solution or from one selected from the library may be requested in the form of figure 3.17. These representations may also be buffered and up to nine of them can be displayed collectively as shown in figure 3.18.

These displays give a useful indication of the growth and decay of intensities in the various spectroscopic bands. Together with the other information obtainable from the solution



```
     SINGLET EXCITED STATES                          PAGE NO.  1
----------------------------------------------------------------------

  ENERGY          X-COMPT.  Y-COMPT.        OSC.  STRENGTH

  4.0048           1.693     .06106           2.0122

  4.2613          -.4984    -.3848             .29583

  5.5402           .86553    .10401            .73709

  5.8837          -.4343    -.1033             .20531

  6.2448           .06449    .19448            .0459

  6.6191           .47982   -.0544             .27021

  6.8457          -.8555    -.3913            1.0607

  7.8729          -.0573     .17912            .04874

  8.5926          -.1586    -.2485             .13074
```

Fig. 3.16

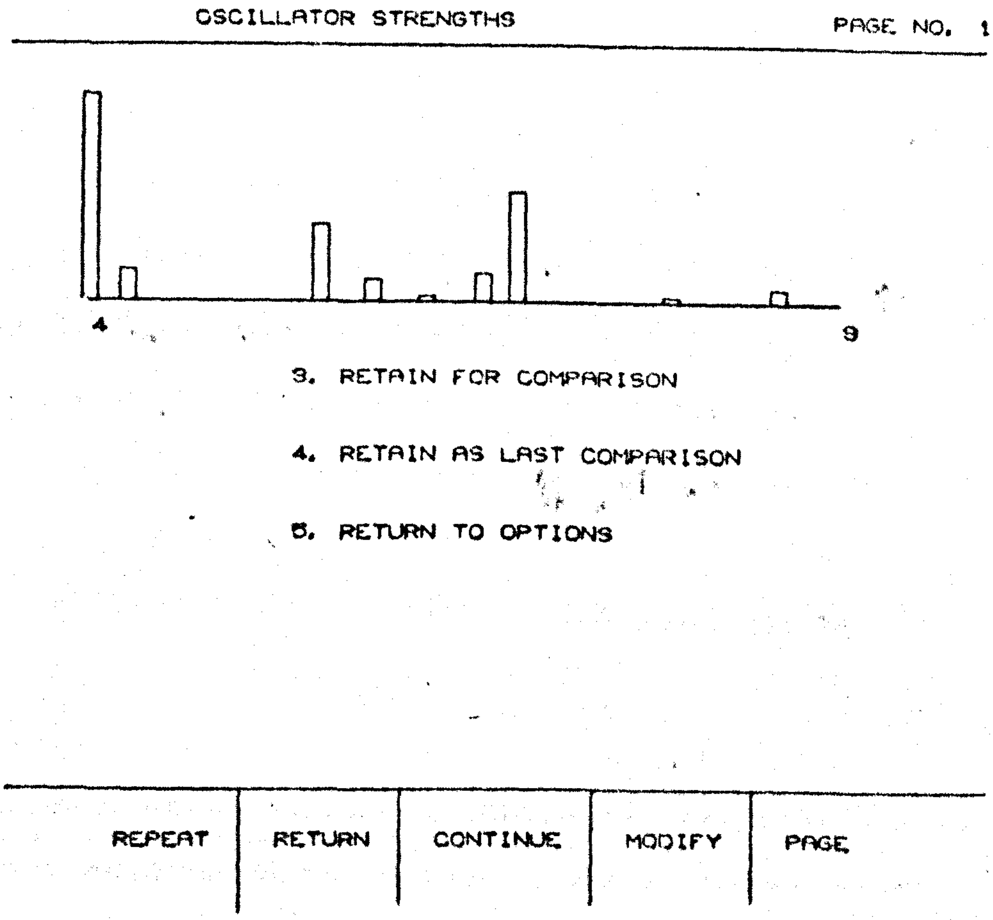
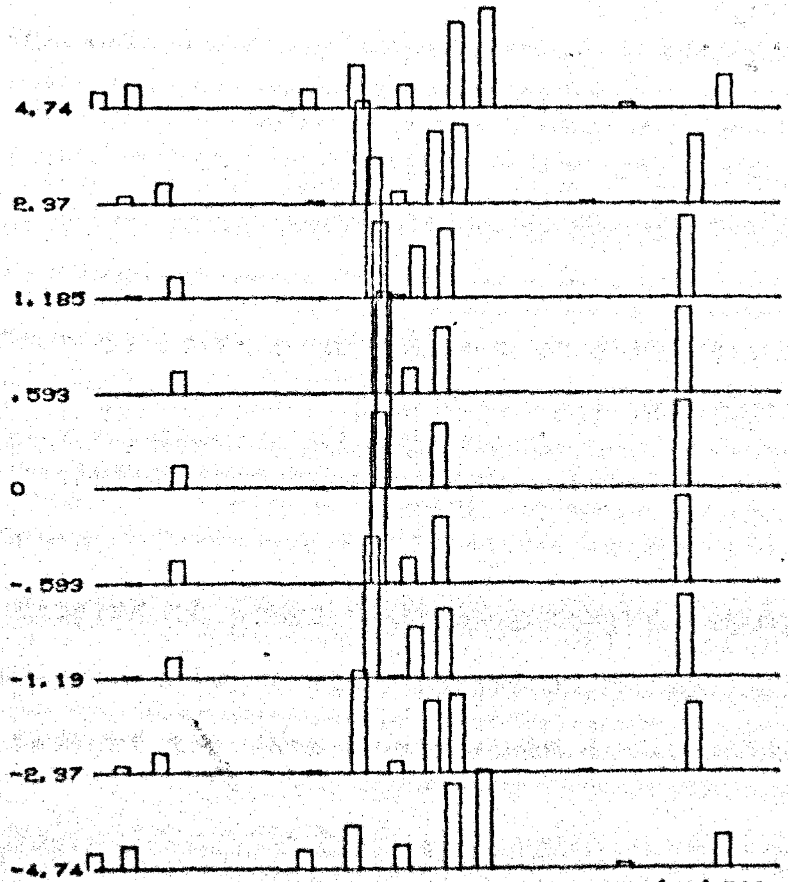


Fig. 3.17



```
FOR PLOT TYPE IN NO. OF EN. LEVEL(12) OR '00' FOR NO PLOT
OR TYPE 99 FOR HARD COPY OF THIS DISPLAY
```

Fig. 3.18

store or already printed out by this stage, the displays offer a reasonably complete account of the properties of the CI solutions.

Finally, the intensities themselves may also be passed on for plotting in level four. This is achieved by typing in the required energy level number for each of the solutions on display in figure 3.18. The independent variable is once again taken to be that modification by which the solutions are distinguished. Alternatively, the intensities may be selected individually, using a similar procedure to that described for energies. Again, this facility is found to be very useful when it is suspected that the automatic procedure might not give the correct set of data points owing to corresponding intensities appearing at different relative positions in successive solutions.

After the completion of any data plot or analysis undertaken in level four there is an automatic return to the source of the data arrays in level three. This enables immediate comparative plots of the same type to be made if required.

3.5 Analysis Section

Level four contains a useful set of data display and analysis routines, together with facilities for storing and recalling data sets and collections of computed curves in their polynomial coefficient form.

A flow diagram of level four is given in figure 3.19.

On entering the level with a pair of arrays (the x and y co-ordinate sets of the data points) the first options presented

LEVEL 4

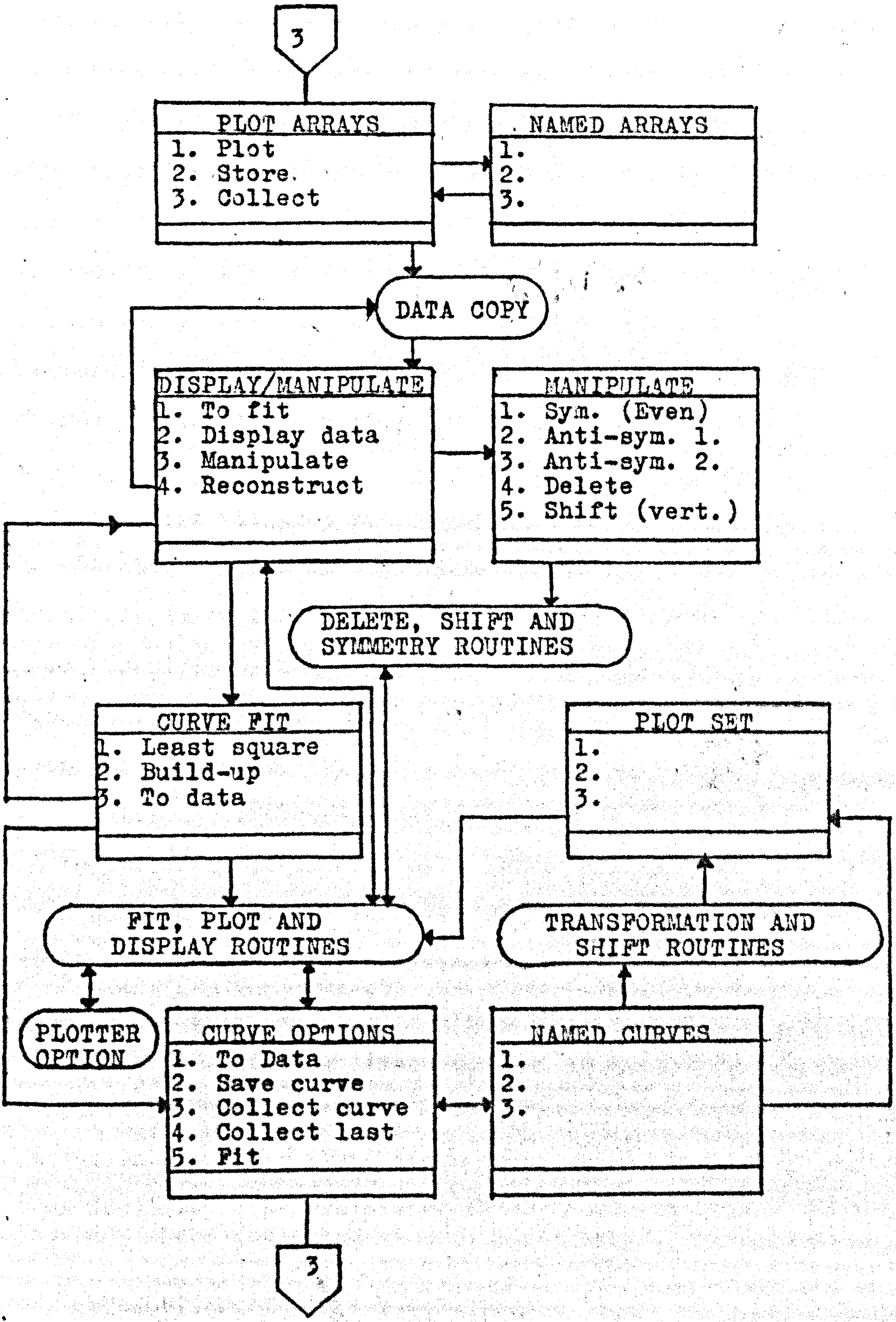


Fig. 3.19

are (i) to proceed at once to the analysis routines or (ii) to save the data for future processing. Data stored at this time must be given a name which is entered into the list appearing in the second frame. The data may be subsequently recalled upon reaching this frame by simply selecting the desired given name from the user-created menu.

Whatever the source of a data set, it is always copied before being subjected to any processing, so that it can be restored later for further use. This option (in the third frame) permits the user to experiment freely with the data, knowing that even if some of the points are displaced or deleted, the original data may always be recovered intact.

Another option at this stage allows for the data points to be displayed on the screen. The desplay includes the x and y axes, complete with numbered tick marks. The origin, its position on the screen and the scales are computed automatically from the data arrays by routines taken from the DISPAC package.

A further optional facility may be utilised before moving on to the analytical routines. Frequently, the data sets arising from quantum chemistry research experiments are known to possess properties of symmetry. Considerable advantage can be taken of this knowledge in terms of storage space and computation time if a means of creating 'image points' is available from data computed on one side of the origin only. The data manipulation option in the third frame leads to a further menu which offers this facility. The operations are brought into effect by a call to

```
SUBROUTINE SYMIT (X,Y,N,KS,YZ,KH)
```

where

X and Y are the co-ordinate arrays for N data points

KS controls the type of symmetry operation

YZ is a vertical displacement.

KH is a second control variable.

For symmetry operations SYMIT is entered with KS = 1 for 'even' data i.e. for every point (x_i, y_i) a new point $(-x_i, y_i)$ is created, KS = -1 for 'odd' data i.e. (x_i, y_i) gives rise to $(-x_i\ -y_i)$ and KS = 0 for 'odd' data not representing a curve through the origin, so that (x_i, y_i) generates $(x_i, 2y_o - y_i)$ where y_o is equal to YZ - whose value must be typed in. Entry with KH $\neq$ 0 shifts the entire set of data vertically by the input distance YZ, thus permitting a vertical movement of data or the subsequently fitted curve for the sake of comparisons, or for re-location at an arbitrary origin. This option and the delete option complete the data manipulation menu.

The delete function and all the data displays, including the output from SYMIT are controlled by

```
SUBROUTINE KRVPT (X,Y,N,IN,KTYPE,AZ,NBUFF,KCV,A)
```

where

X and Y are the co-ordinate arrays for N data points,

IN is the degree of the polynomial to be plotted if required,

KTYPE indicated the type of polynomial,

AZ is the a_o term (constant) of the polynomial,

NBUFF is the display code buffer,

KCV indicates the type of display,

A is the array of polynomial coefficients.

A flow diagram of KRVPT is given in figure 3.20. When used to

SUBROUTINE KRVPT

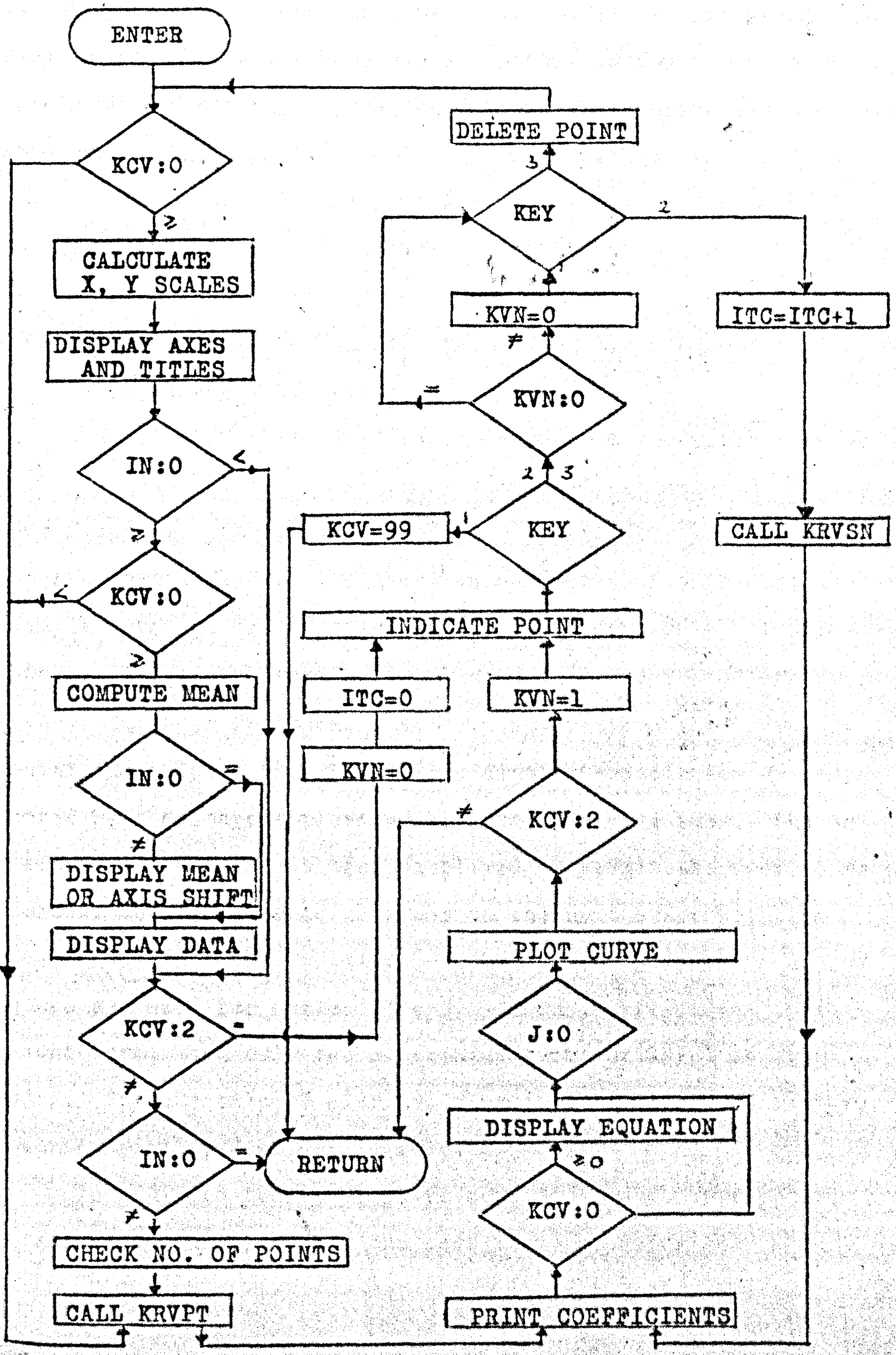


Fig. 3.20

plot curves, KRVPT is usually included in a call to subroutine GRAFT (described later) and the values of IN, KTYPE, and KCV are interactively set to produce the desired results from KRVPT. The range of settings of IN and KCV and their effects are as follows

IN = J, KCV = 1, least square fit of degree J with full display

IN = -J', KCV = 1, second least square fit, degree J' on same axes

IN = 0, KCV = 0, data and axes only

IN = J, KCV = -1,-2,-3,-4 or -5, up to 5 curves from curve store displayed simultaneously.

The first two combinations are the standard settings originating in subroutine GRAFT. The third is the means of obtaining the simple data and axes display on entry to level four, as described above. The fourth setting is used to activate the delete function. The user positions the tracking cross on the redundant point and selects the appropriate display console key as indicated by a message appearing above the data and axes. The new reduced set of data is then displayed to permit the user to make further deletions or to progress to the next stage with the new data. The final settings of the control parameters listed above are used for curves already stored in polynomial coefficient form, when only the plotting section of KRVPT is to be used. For the sake of clarity, a maximum of five such simultaneously displayed curves is allowed.

In addition to the displays outlined above, appropriate messages appear to enable the user to move comfortably and speedily through the system.

The polynomial curve to be displayed is evaluated from its coefficient form at one-tenth inch intervals along the x-axis by a rapid nested multiplication and is actually plotted as about one hundred line segments. This is not noticeable to the eye and the plotting also appears to be instantaneous. The equation of the polynomial is given above the curve and is indicated by a symbol which corresponds to one at each end of the displayed curve. This is to distinguish curves and equations in a multiple display. A manual over-ride of the automatic scaling routines is provided. This is useful when two or more curves are to be simultaneously displayed and are such that the automatic routines would compute incompatible scales and axes, possibly resulting in a curve or curves being omitted from the display.

Two routines, KRVFT and KRVSN, are at present included for computation of the actual polynomial coefficients. They are called from within KRVPT but their specifications must first come from

```
      SUBROUTINE GRAFT (N,X,Y,NBUFF,KCV,AC,JC)
```

where

X and Y are the co-ordinate arrays for the N data points

NBUFF is the display code buffer

$$\left.\begin{aligned} KCV &= 1 \text{ for least-square fit} \\ &= 2 \text{ for polynomial build-up} \end{aligned}\right\} \text{ set in main program}$$

AC is the set of computed polynomial coefficients

JC is the number of coefficients in AC

A flow diagram of GRAFT is given in figure 3.21.

Immediately GRAFT is entered, a message appears giving the

SUBROUTINE GRAFT

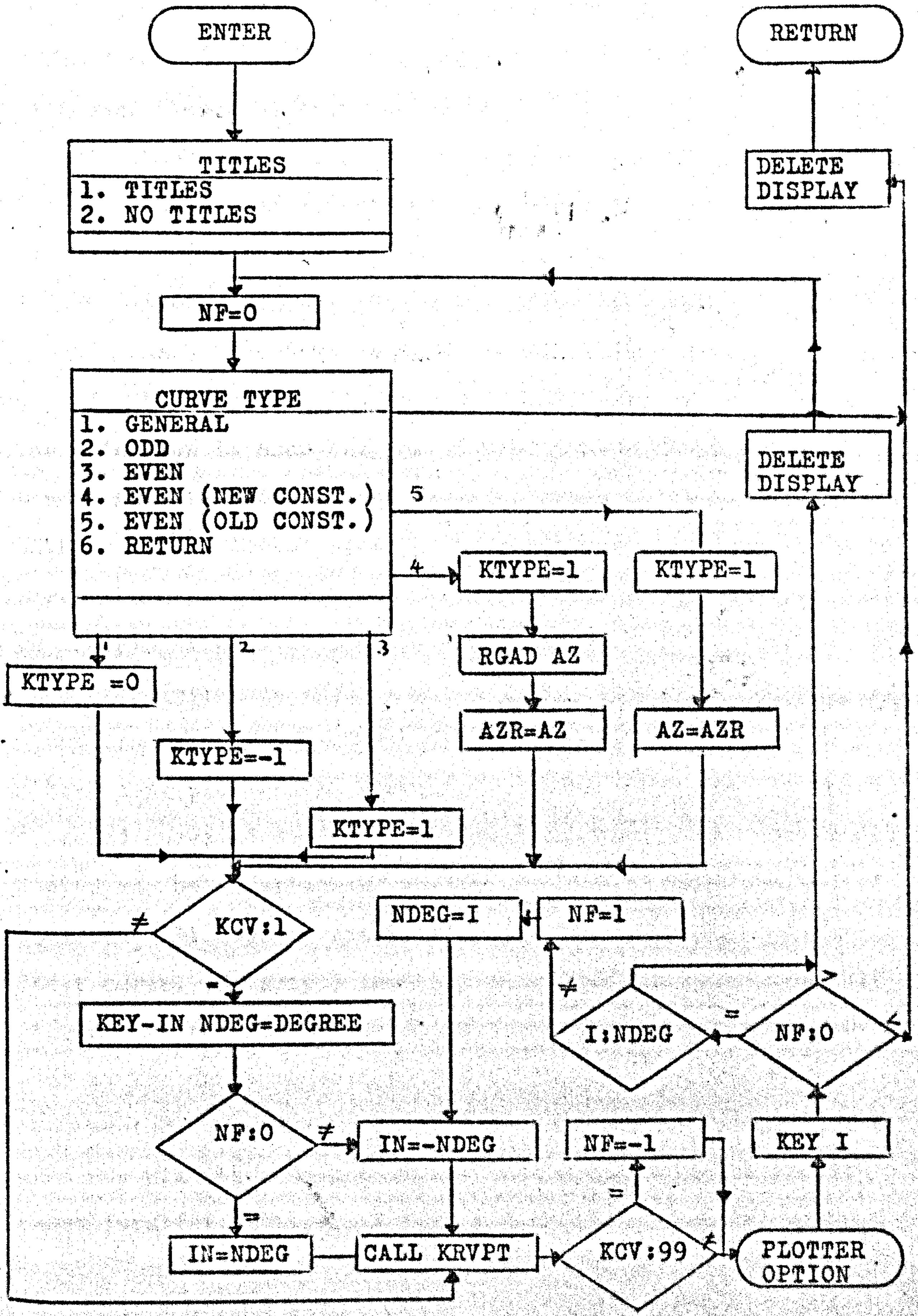


Fig. 3.21

user the option of typing in titles for the forthcoming graph and the two axes. These would appear in all displays containing axes within the current call to GRAFT. Next follows a request for the user to indicate which type of polynomial is to be found. The choice is made from

1. General - all terms computed
2. Odd - coefficients of odd powers only
3. Even - coefficients of even powers only
4. Even - but with a_o specified by the user
5. As 4. - but where a_o is recalled from memory
6. Exit from GRAFT, return to main program.

The selection is made via the display console keys and the result gives a value to the variable KTYPE which is used in KRVPT. If the 'least square' curve fitting procedure is to be used, the user must now specify the degree of the fitting curve by choosing the corresponding key between 1 and 8. Control is then transferred to KRVPT and the calculations and the display operation take place. There is a return to GRAFT at which point a hard copy plot of the curve etc., may be obtained, or where a second curve of different degree from that curve already displayed may be superimposed on the first for comparison. Its equation will also be displayed beneath the equation of the first curve. Finally a re-start with the same data, possibly in order to compute curves of different types or degree, may be made by the dummy request of asking for the last curve to be re-computed. However many curves are produced in GRAFT, the last one will be returned to the main program in its coefficient form for storage and possible future reference, without the need for its re-computation.

The coefficients of the best fitting polynomial, according to the least-square criterion, are computed in

SUBROUTINE KRVFT (X,Y,N,K,ND,A,H,KTYPE,AZ)

where

X and Y are the input data arrays for N data points

K is the increment between elements of X and Y (normally equal to 1)

ND is the required degree of the polynomial

H is the mean value of the elements in X

KTYPE = -1 for an 'odd' fitted function

0 for a general function

+1 for an 'even' fitted function

AZ is the a_o term of the polynomial.

The standard least-square procedure as given in Froberg {9}, for example, has been modified in this subroutine to deal as efficiently as possible with data having the special properties frequently encountered in quantum chemistry research.

The fundamental requirement is to minimize the quantity

$$S = \sum_{j=0}^{n} (a_m x_j^m + a_{m-1} x_j^{m-1} + \ldots + a_o - y_j)^2$$

where (x_j, y_j) for $j = 0 \ldots n$ is the set of n+1 data points and $a_m, a_{m-1}, \ldots, a_o$ is the set of m+1 coefficients of the fitting curve.

The necessary conditions for a minimum are

$\frac{\partial s}{\partial a_k} = 0$ for $k = m, m-1, \ldots, 0$ leading to the so called normal equations which, with the notations

$$d_k = \sum_{j=0}^{n} x_j^{\ k} \text{ and } b_k = \sum_{j=0}^{n} x_j^{\ k} y_j$$

can be conveniently expressed as

$$\begin{aligned} d_{2m} a_m + d_{2m-1} a_{m-1} + \ldots + d_m a_o &= b_m \\ d_{2m-1} a_m + d_{2m-2} a_{m-1} + \ldots + d_{m-1} a_o &= b_{m-1} \\ \vdots \qquad\qquad\qquad\qquad & \quad \vdots \\ d_m a_m + d_{m-1} a_{m-1} + \ldots + d_o a_o &= b_o \end{aligned} \qquad -(1)$$

or, in matrix notation, as

$$DA = B \qquad -(2)$$

Setting KTYPE = 0 on entry to subroutine KRVFT initiates a full generation of D and B. The set of equations DA = B is then solved for A by Gauss-Jordan elimination in a standard subroutine GAUJOA.

The special cases for which modifications to this procedure have been made are

(i) data which is anti-symmetrical about the vertical axis, for which a polynomial approximation of odd powers only is required, (KTYPE = -1). It is assumed that the fitting curve will pass through (0,0) in this situation. This tends to be the case in practice, especially since the origin is frequently one of the data points - representing an observation of the unperturbed state. If, however, the data indicates an anti-symmetric curve, which obviously does not pass through the origin, then a vertical transformation of the data can be made before fitting, as described earlier using subroutine SYMIT, with a corresponding adjustment to the constant term of the polynomial subsequently obtained. To ensure the appearance of odd powers only, the arrays D and B are generated in the forms

$$D = \begin{bmatrix} d_{2m} & 0 & d_{2m-2} & 0 \ldots & d_{m+1} & 0 \\ 0 & 0 & 0 & 0 \ldots & 0 & 0 \\ d_{2m-2} & 0 & d_{2m-4} & 0 \ldots & d_{m-1} & 0 \\ 0 & 0 & 0 & 0 \ldots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ dm+1 & 0 & d_{m-1} & 0 \ldots & d_2 & 0 \\ 0 & 0 & 0 & 0 \ldots & 0 & 0 \end{bmatrix} \quad \text{and } B = \begin{bmatrix} b_m \\ 0 \\ b_{m-2} \\ 0 \\ \vdots \\ b_1 \\ 0 \end{bmatrix}$$

by an initial setting of all the elements to zero. The later summations are performed for only those non-zero d_k and b_k indicated above.

(ii) data symmetrical about the vertical axis, for which a polynomial of even powers only is required, (KTYPE = +1). Hence D and B have the forms

$$D = \begin{bmatrix} d_{2m} & 0 & d_{2m-2} & 0 \ldots & 0 & d_m \\ 0 & 0 & 0 & 0 \ldots & 0 & 0 \\ d_{2m-2} & 0 & d_{2m-4} & 0 \ldots & 0 & d_{m-2} \\ 0 & 0 & 0 & 0 \ldots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 \ldots & 0 & 0 \\ d_m & 0 & d_{m-2} & 0 \ldots & 0 & d_o \end{bmatrix} \quad \text{and } B = \begin{bmatrix} b_m \\ 0 \\ b_{m-2} \\ 0 \\ \vdots \\ 0 \\ b_o \end{bmatrix}$$

In both of cases (i) and (ii) the D matrices are first compacted to the respective matrices of normally non-zero elements, possessing dimensions (i) $\frac{m+1}{2}$ and (ii) $\frac{m+2}{2}$ respectively. Corresponding reductions are made to B before entry into subroutine GAUJOA. On the return from GAUJOA, the array A of computed coefficients is re-expanded to dimension m+1 by the insertion of zero elements, in the appropriate even or odd positions respectively, before being passed to the plot routine KRVPT in the form

$$(a_m, a_{m-1}, \ldots, a_1, a_o)$$

(iii) data as in (ii) but which corresponds to a curve intersecting the vertical axis at a point other than the origin. If there is a data point on this axis (e.g. corresponding to an observation of the unperturbed state), then clearly the fitting curve must be computed to pass through this point, utilising and displaying its inherent accuracy. There is a danger when using the standard least square procedure of "missing" such a point with the computed curve, so, to overcome this problem, there is incorporated into KRVFT a means of interactively specifying "a_o", the constant term in the polynomial. This is remembered for as long as required so that, once found, it can be re-used for fits of different order m. The least-square computation is modified in such a way that, in effect, the a_o term is constrained to remain at the value stipulated and the optimal curve is computed using the off-axis data points. The mathematical consequence of predetermining a_o is to remove one of the conditions, namely $\frac{\partial S}{\partial a_o} = 0$. Hence one of the normal equations (1) and the corresponding last rows in arrays D and B also disappear. The contribution of a_o in the other equations is taken care of by adjusting the non-zero elements b_k of B to

$$b_k' = b_k - d_k . a_o \text{ for } k = m, m-2, \ldots, 3.$$

D and B are then compacted as before and a similar procedure is followed in the derivation of A.

All the computations in this subroutine are performed using elements of the data array X measured relative to the computed mean value H of these elements. This has three main advantages

(a) Rounding error is minimised when computing the sums of squares d_k and b_k.

(b) A data point actually at $x_j = H$ will have a new x-co-ordinate equal to zero and can be omitted from the summations d_k and b_k - giving a slight saving in computational effort.

(c) Since H is computed in KRVPT it can be modified artificially, giving an opportunity for translating the computed curve in a horizontal direction.

The disadvantages of polynomial curve fitting by the least square method must be recognised. The normal equations are notoriously ill-conditioned if m is at all large, and serious loss of accuracy can result if the method is used over-enthusiastically. The observable symptom is of a curve which passes fairly closely to all the data points but performs unrealistically inbetween and beyond the points. However the method does have the advantage of being very rapid, particularly when economy measures such as those described earlier are adopted. It takes only a second or two, both to compute and to display the curve and its equation using the present routines, there being no noticeable time difference for curves of different degree. Also, the present system permits progressively higher order curves to be found and examined in pairs for the same data. The eye can quickly detect a wayward curve, so the most realistic, well-fitting curve can easily be selected from those found. For the majority of data sets in the present context, satisfactory fits of up to degree six can be obtained using about nine data points. A typical least-square curve plot taken from the display is given in figure 3.22.

As a safeguard, a message appears on the screen if insufficient points are available for a fit of the requested degree and the computation is not commenced.

For more complex data the method undoubtedly has its drawbacks but the data derived from the approximate models of quantum chemistry are reasonably well behaved and no severe problems are usually encountered. However, in addition to showing how well the least square method can work if properly used, interactive graphics does provide a fascinating insight into the problems of attempting to fit polynomials of too high a degree. The danger of formally adopting such a curve for analytical purposes, when it is a poor representation in regions not close to the data points, can be avoided if the curve is first inspec-

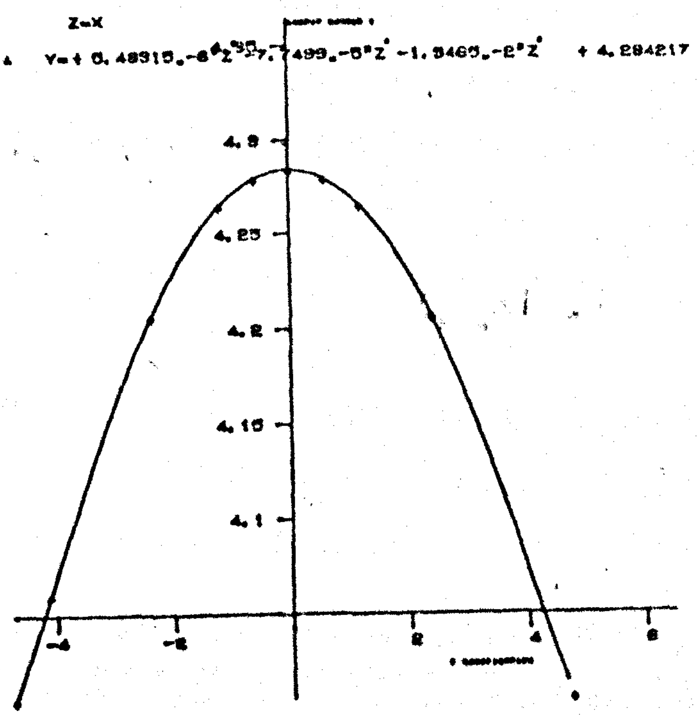


Fig. 3.22 (a, free)

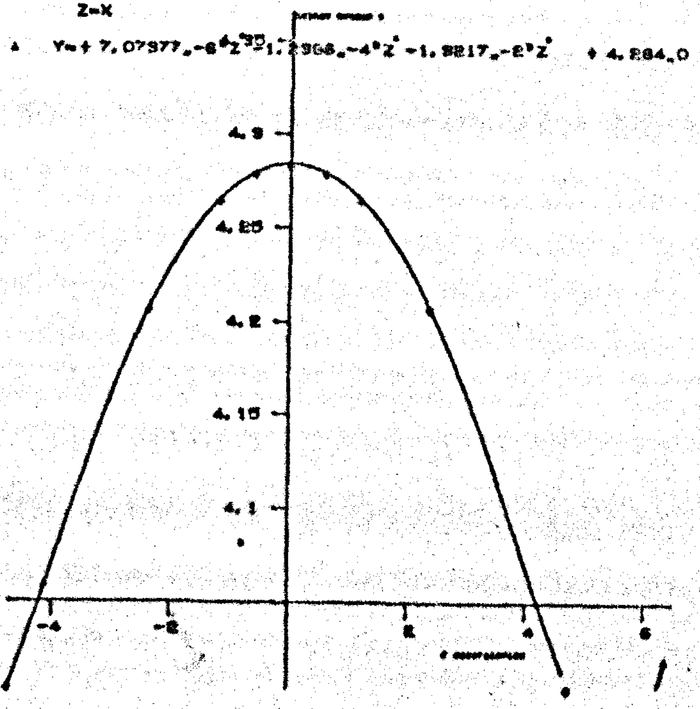


Fig. 3.23 (a, fixed)

ted visually as in the present system.

The severity of the ill-conditioning of the normal equations depends to a large extent upon the distance of the data points from the origin. To get sufficiently close to distant points, the curve may also be pulled away from the inherently more accurate inner points. Hence it can be worthwhile (particularly if coefficients of only first and second order terms are required) to discount the extreme points and settle for a better fit, possibly of lower order, with the innermost points only. The inclusion of the delete facility described earlier enables this to be accomplished.

The system can be readily extended to include more sophisticated methods such as those given by Hayes, {10}, but it is acknowledged that these sometimes give only marginal improvement over more primitive methods when the data sets are well behaved. The improvement needs to be significant to repay the extra cost in terms of programming effort, storage space and computation time. The last two factors are particularly important considerations in interactive graphical work.

However, some methods undoubtedly have advantages over others for certain types of data and, if further methods are made available as options, interactive graphics may be profitably used for making comparative examinations of the relative performances of the methods supplied.

A second curve fitting method is at present included in the system. This method recognises the fact that only the first and/or second polynomial coefficients are sometimes required; i.e. a_0 and a_2, the intercept and curvature for an even function or the slope at the origin a_1 for an odd function. In effect the method synthesises or builds up an odd or even polynomial

$$y = a_0 + a_1 x_1 + a_2 x^2 + \ldots$$

term by term, using

SUBROUTINE KRVSN (X,Y,N,A,KTYPE,AA)

where

X and Y are co-ordinates of a single data point

N is a count of the coefficients found

A is the computed array of coefficients

KTYPE = -1 for an odd function

= +1 for an even function

AA is a working array

Entry to KRVSN is made within subroutine KRVPT, the tracking cross mechanism being used once again to indicate specific data points. The first point indicated will establish, for an odd function, an approximation to the gradient at the origin or, for an even function, the constant term, a_0. The technique is, therefore, to work outwards from the origin when indicating points. The second point, (x_2, y_2), generates a_3 and a_2 for odd and even functions respectively from the expressions

$$a_3 = (y_2 - a_1 x_2)/x^3 \text{ and } a_2 = (y - a_0)/x^2$$

where a_0 and a_1 are values already found. The process may be continued up to degree seven or degree six for odd and even functions respectively. The intermediate zero coefficients are inserted before the complete string of coefficients is returned to KRVPT in the order

$$a_m, a_{m-1}, \ldots a_1, a_0$$

to correspond with the ordering established in the least square subroutine KRVFT. The curve and its equation are automatically displayed at each step. An example of a curve computed in this way is given in figure 3.24. The technique is effective for producing low order coefficients and is especially accurate when good points close to the origin are used.

Curves obtained by any method are printed out and may be stored in their polynomial coefficient form as a result of options specified in the final section of level four. From the list of curves so stored, further individual selections may be made and the functions may be subjected to linear or non-linear transformations before being added to another buffer for simultaneous display. At this point optional facilities for interactively modifying scaling factors may be usefully employed. This buffering procedure safely maintains the original curves and, at the same time, permits free experimentation and analysis to be undertaken.

Finally, on completion of any analytical work in the fourth level, control is passed back to the source of the data used. From here, more data of the same type can be examined or a backtrack or sideways move to another section of the program may be made as desired.

3.6 Data Storage and Retrieval

Two main types of permanent data file need to be set up on backing store for use by the interactive graphics system. These are (i) the file of menu texts and (ii) the library of computed solutions. Each type must be structured in such a way that accessing and updating operations may be carried out rapidly and effectively.

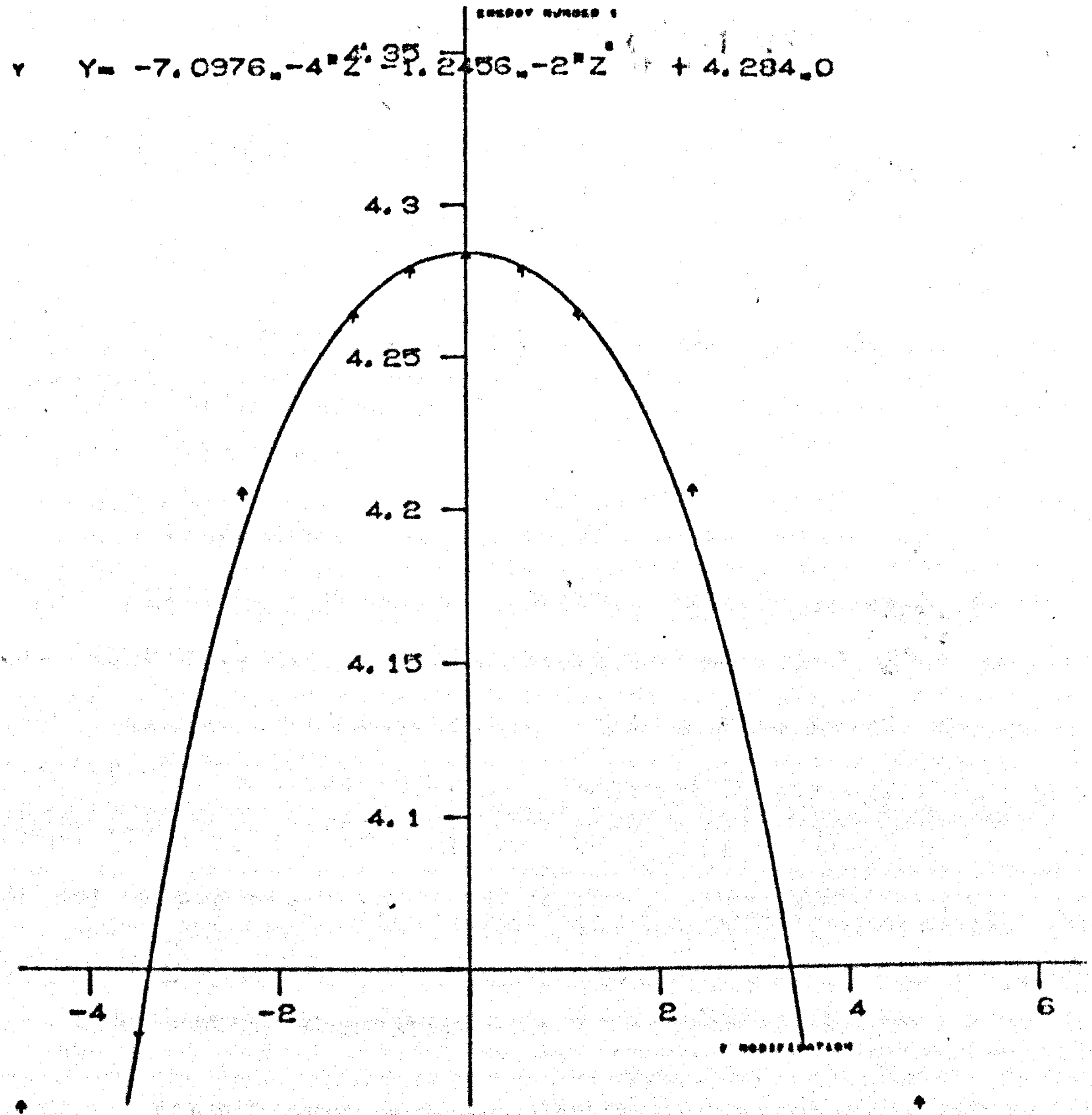

Y
Y= -7.0976.-4*Z -1.2456.-2*Z + 4.284.0
ENERGY NUMBER
4.35
4.3
4.25
4.2
4.15
4.1
-4
-2
2
4
6
MODIFICATION

Fig. 3.24

3.6.1 Menu Text File

The current structure of the menu text file is as shown in figure 3.25.

A subroutine DFILT sets up a permanent disc V-file with sufficient space allocated for textual information associated with each of the four separate main program levels. Each level can possess up to 15 frames (menus) containing up to 17 lines (items), where each menu item may be up to 40 characters (5A8 format) in length.

Initial input to this file takes the form of a data record for each level indicating the number of menu items in each frame at that level, followed by the texts, one menu item per record, for that level.

The subroutine

```
FWRDS (WDS, LN, NW, NXTFR)
```

is used prior to each call to subroutine MENU in order to locate that frame with number NXTFR (specified as a result of a user action) within level number LN. On exit from FWRDS, the menu texts of the required frame are assigned to the array WDS (dimensioned (17,5)), and NW contains the number of items in that menu. WDS and NW are then used to specify the menu displayed in subroutine MENU.

An up-dating subroutine

```
RFWRDS (WDS, LN, NW, NR)
```

is called if, on exit from subroutine MENU, it is detected (MOD≠0) that a modification has been made in core to the displayed frame. The array WDS contains the modified menu, which corresponds to

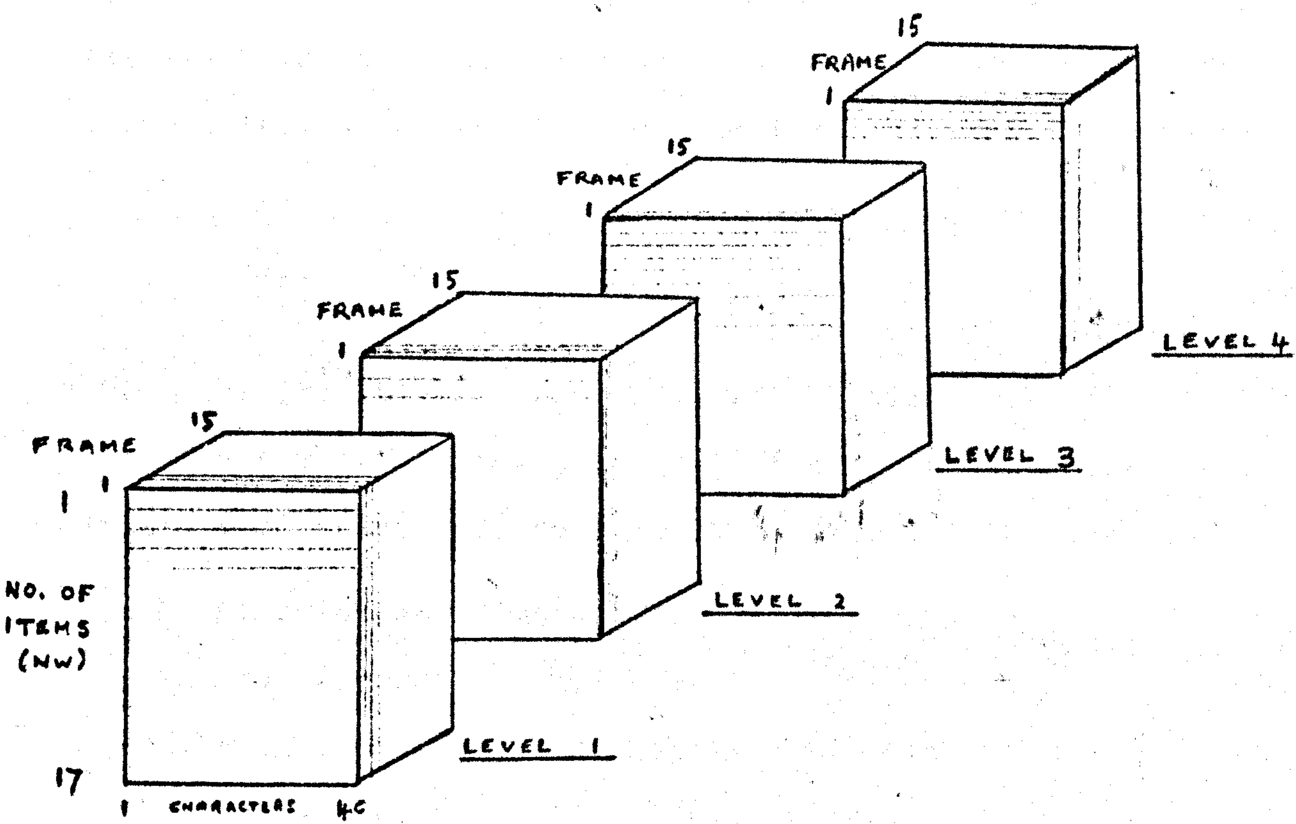


Fig. 3.25

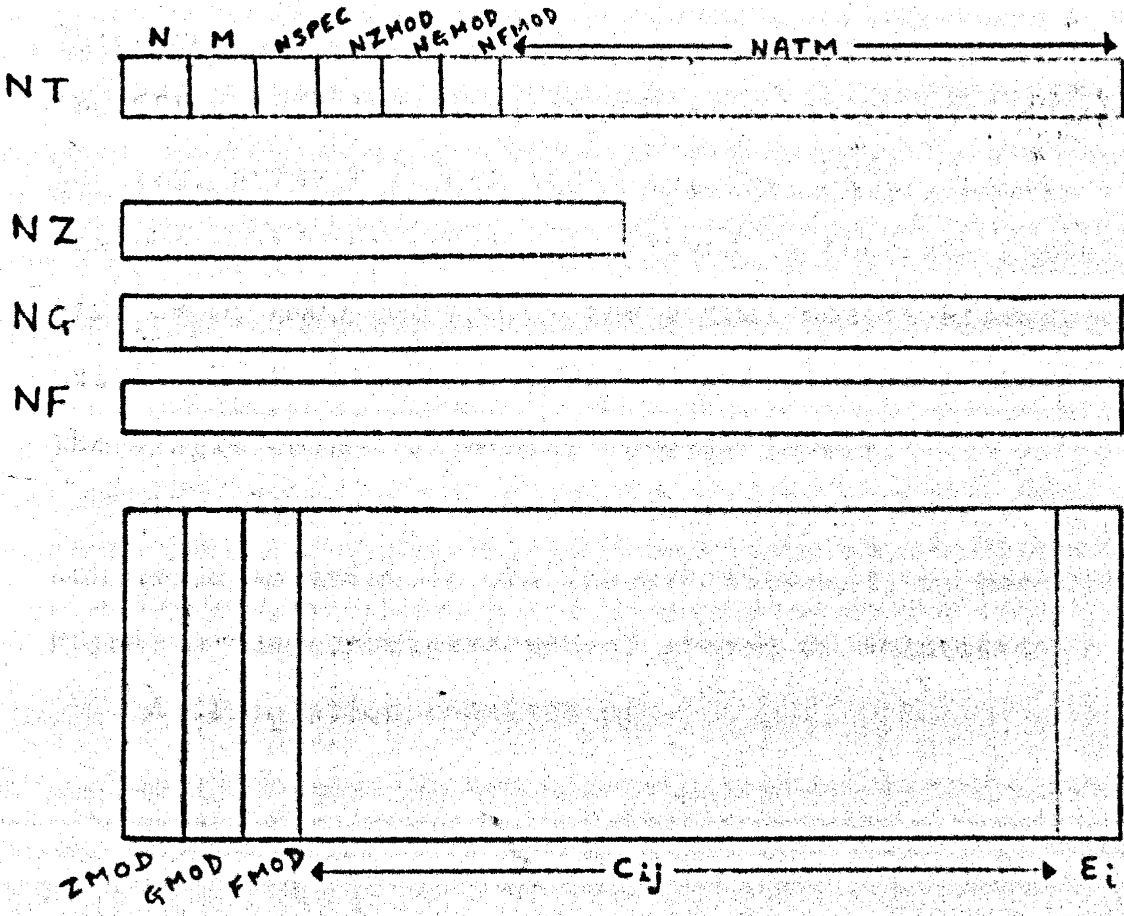


Fig. 3.26

frame number NR in level LN, and which at this point in time contains NW menu items. The function of RFWRDS is effectively to re-write, on permanent file, the first NW menu items of the specified frame.

3.6.2 Solution File

The structure of a typical SCF solution is shown in figure 3.26. The initial data record NT which, along with the solution reference number defined in section 3.3, forms an entry in the directory of solutions, contains the following information

N no.of atoms in molecule

M no. of occupied orbitals

NSPEC = 0 if no CI solutions available
= no. of CI solutions, otherwise.

NZMOD, NGMOD, NFMOD i.e. numbers of Z, G and F modifications

NATM - array of grid co-ordinates, or other geometry specification

Three more integer records follow, namely NZ, NG and NF containing the SCF matrix locations of the respective modifications. Finally the real array W (dimensioned (N, N+4, MKSL), where MKSL is the maximum number of solutions allowed in the set) contains columnwise ZMOD, GMOD and ZMOD - the actual modifications, where they exist, the N columns of LCAO molecular orbital coefficients, and the single column of orbital energy levels.

The solution reference number NSOL is used to locate the nominated solution in the library file and, if NSPEC ≠ 0, to point to the associated set of stored CI solutions.

A CI solution consists of -

MINK - no. of replacement configurations

SMINK - no. of elements retained in stored vectors

NGMOD, NFMOD - no. of G and F modifications to ground state

NG, NF - locations of modifications in SCF matrix

GMOD, ZMOD - the modified values

LL - vector of occupied levels involved in replacements

LH - vector of unoccupied levels in replacements

H - state energy vector

OSC - oscillator strength vector

The early applications of the system made use of named solutions stored in the user library and referenced by channel numbers associated with the solution numbers defined as in section 3.3. However, more recent applications have experimented with more sophisticated data structures, based on V-files, similar to that described for menu texts in section 3.6.1. There is scope for further development work on the organisation of the computed solution library file. This will become more important as the quantity of stored solutions increases with time.

3.7 References

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{2} Pople, J A and Beveridge, D L - "Approximate Molecular Orbital Theory", McGraw-Hill (1970)

{3} Quantum Chemistry Program Exchange, Department of Chemistry, University of Indiana, Bloomington, Ind.

{4} Sturdy, M D and Collis, P G - DISPAC/PLOPAC, Computer Centre Program Library Number KU0032, University of Keele

{5} 4100 Manual, Vol 2, Part 16, Section 3, ICL (1969)

{6} Daniel, P T - "Process Plant Design", Computer Graphics 70 Conference, Brunel University, 1970

{7} Pariser, R and Parr, R G - J Chem. Phys., 21, 466 (1953)

{8} Pariser, R and Parr, R G - J Chem. Phys., 21, 767 (1953)

{9} Froberg, C-E - "Introduction to Numerical Analysis", Addison-Wesley (1965)

{10} Hayes, J G (Ed) - "Numerical Approximations to Functions and Data", Athlone Press (1970)

CHAPTER FOUR

ANALYSIS OF GROUND STATE PROPERTIES

This chapter describes the application of the graphics system to investigations of properties of ground state solutions. The methods currently incorporated within the system, their associated parameter schemes, and details of how these are brought into practical effect are first covered briefly. There follows a short discussion on the economic planning of SCF ground state computations, and the procedure outlined here is adopted in the practical experiment, chosen by way of example, which is described next. The description takes the form of a step by step account of the use of the graphics system to interactively control the nomination, calculation and display of properties of SCF solutions for aniline. The results, expressed in graphical form, are briefly analysed in a subsequent section, and the complete set of curves generated in the experiment is presented at the end of the chapter.

4.1 Methods and Parameters

At the present time only the Huckel and the P-P-P SCF methods for describing ground states of π electron systems are available as part of the interactive graphics system.

The Huckel method has elsewhere been extended with some success to deal with σ electrons, {1}, and it would be relatively straightforward to include it in the graphics system in this form. However, although the method has proved of interest to experimentalists, it is generally true to say that SCF methods offer greater reliability and can be performed rapidly on modern computers, so further developments of methods within the interactive computing system are likely to be in the form of refinements and extensions to SCF procedures. As a result, several different SCF parameter schemes are already included.

Brief accounts of the methods used for interactively specifying parameters in both Huckel and SCF calculations will now be given.

4.1.1 Huckel Calculations

When the geometry of the molecule has been established by one means or another, and the Huckel method has been selected from the menu of available methods, the basic Huckel matrix is automatically set up. This consists of a leading diagonal filled with zeros i.e. all coulomb integrals $\alpha_\mu = \alpha = 0$; off-diagonal elements are set equal to -1.0 for neighbours, and to zero for non-neighbours i.e. the resonance integral $\beta_{\mu\nu} = -1.0$. Then, α and β for adjacent carbon atoms are normally taken as the zero and unit of energy, respectively, and any desired modifications to either α_μ or $\beta_{\mu\nu}$ are expressed in multiples of β, by effectively inputting s_μ or $t_{\mu\nu}$, where

$$\alpha_\mu = \alpha + s_\mu \beta \qquad -(1)$$

and

$$\beta_{\mu\nu} = t_{\mu\nu}\beta \qquad -(2)$$

This is achieved in practice by following the instructions given in the display -

```
HUCKEL MATRIX MODIFICATIONS

TYPE IN:  I,J (2I2)
   THEN:  H(I,J) (F0.0)

(TYPE 0000 IF NO FURTHER MODS)
```

Fig. 4.1

In this chapter, frequent reference will be made to displays of menus and other forms of textual information which appear on the screen during the course of interactive experiments. Although these can be plotted, as illustrated by the photographically reduced examples given in the previous chapter, it is not normal practice to plot displays, other than those containing curves and diagrams. For this reason, and also to simplify and clarify the discussion, menus etc. will henceforth be represented within the text, in the manner of figure 4.1.

Modifications need only be made to elements in the lower half of the matrix (I>J), since a complementary symmetrical modification is automatically made.

After the user has indicated that no further Huckel matrix modifications are required, the display represented in figure 4.2 appears. This presents the opportunity to modify the effective core charge Z_μ at an atom from the assumed unit value. The nitrogen atom in aniline, for example, contributes two electrons to the π-electron system, and this would be specified here.

```
Z MODIFICATIONS

TYPE IN:  K    (I2)
   THEN:  Z(K) (F0.0)

(TYPE 00 IF NO FURTHER MODS)
```

Fig. 4.2

All modifications are recorded on the line printer, to precede the printed output of the solution etc.

On completion of the modifications, the Huckel matrix is diagonalised. The solution and quantities derived from it may then be selected for display and analysis as described for SCF solutions in the previous chapter. The parent molecule originally specified is retained until it is replaced, and may be recalled to be subjected to further modifications without having to be re-generated.

4.1.2 SCF Calculations

The general procedure for specifying parameters and modifications in SCF calculations has already been described in chapter three. On reaching the frame headed 'SCF PARAMETERS' in the new solution route of level two (see figure 3.10), the user initiates a branch to specify either γ integrals or β integrals. Currently a selection may be made from three parameter schemes for γ and from four for β. The γ approximations are

(1) P-P-P

For interatomic distances $r_{\mu\nu}$ exceeding 2.80 Å, Parr {2} , and Pariser, {3}, proposed the formula

$$\gamma_{\mu\nu} = \frac{e^2}{2r_{\mu\nu}} \quad (1+\{\frac{D_\mu - D_\nu}{2r_{\mu\nu}}\}^2)^{-\frac{1}{2}} + (1+\{\frac{D_\mu + D_\nu}{2r_{\mu\nu}}\}^2)^{-\frac{1}{2}} \qquad -(3)$$

based upon the classical interaction of two uniformly charged spheres of diameter

$$D_\mu = \frac{4.597}{Z_\mu} \times 10^{-8} \text{ cm} \qquad -(4)$$

where Z_μ is the effective nuclear charge for the $2p_z$ atomic orbital ϕ_μ.

For large distances of separation, when $r_{\mu\nu} >> D_\mu$, equation (3) reduces to the form

$$\gamma_{\mu\nu} = 14.4/r_{\mu\nu} \qquad -(5)$$

This expression supplements the empirically derived values

$$\gamma_{11} = 11.35,\ \gamma_{12} = 7.19,\ \gamma_{13} = 5.77,\ \gamma_{14} = 4.97 \qquad -(6)$$

obtained for hydrocarbons by Parr and Pariser, {4}, for the largest $\gamma_{\mu\nu}$ integrals. Both (5) and (6) are used in the present system, with $r_{\mu\nu}$ calculated from atomic co-ordinates.

(2) Nishimoto-Mataga, {5}

This approximation for $\gamma_{\mu\nu}$ takes the form

$$\gamma_{\mu\nu} = e^2/(a_{\mu\nu} + r_{\mu\nu}) \qquad -(7)$$

where

$$1/a_{\mu\nu} = \tfrac{1}{2}(\frac{1}{a_{\mu\mu}} + \frac{1}{a_{\nu\nu}}) \qquad -(8)$$

with

$$a_{\mu\mu} = e^2/\gamma_{\mu\mu} \qquad -(9)$$

The one centre electron repulsion integrals are calculated using the Pariser expression, {6}, namely

$$\gamma_{\mu\mu} = I - A \qquad -(10)$$

where I and A are, respectively, the ionization potential and the electron affinity at the μ-th atom. Values of parameters used are given below (based on data of Hinze and Jaffe, {9})

	I_μ(eV)	$\gamma_{\mu\mu}$(eV)
C^+	11.16	11.13
N^+	14.12	12.34
N^{++}	26.70	17.44
O^+	17.70	15.23
O^{++}	32.9	21.53

Table 4.1

In some recent experiments, the value of $\gamma_{\mu\nu}$ given by (7) has been adjusted at each iteration by assuming the following relation between bond distance and bond order

$$r_{\mu\nu} = D_o + D_1 P_{\mu\nu} \qquad -(11)$$

with values of D_o and D_1 as given below

	D_o(Å)	D_1(Å)
C-C	1.517	-0.180
C-N	1.451	-0.180
C-O	1.410	-0.180

Table 4.2

(3) Ohno-Klopman, {7,8}

A third alternative scheme for $\gamma_{\mu\nu}$ sets

$$\gamma_{\mu\nu} = e^2/\left(r_{\mu\nu}{}^2 + e^2 b_{\mu\nu}{}^2\right)^{\frac{1}{2}} \qquad -(12)$$

where $$b_{\mu\nu} = \tfrac{1}{2}\left(\frac{1}{\gamma_{\mu\mu}} + \frac{1}{\gamma_{\nu\nu}}\right) \qquad -(13)$$

The same values for $\gamma_{\mu\mu}$ are used both here and in the Nishimoto-Mataga approximation. The appropriate values from the stored table are automatically assigned when carbon atoms are interactively replaced in the grid structures, as described in the previous chapter. Thus, on selection of either method (2) or method (3) above, the calculations of $\gamma_{\mu\nu}$ can take place according to expressions (7) or (12) respectively.

The methods for specifying $\beta_{\mu\nu}$ are

(1) P-P-P Approximation

The resonance integral $\beta_{\mu\nu}$ is here taken to be zero for all orbitals except those on neighbouring atoms, and this nearest neighbour value, obtained by Parr and Pariser at the same time as the $\gamma_{\mu\nu}$ values given in (6) is set at the constant value

$$\beta = -2.37 \qquad -(14)$$

(2) Mulliken Overlap Approximation

Mulliken, {10}, has proposed that $\beta_{\mu\nu}$ be proportional to the overlap integral $S_{\mu\nu}$, i.e.

$$\beta_{\mu\nu} = kS_{\mu\nu} \qquad -(15)$$

When this scheme for β is selected, a message appears on the screen, requesting a value for k to be typed in, with an optional default to a value given by

$$k = \frac{\beta}{S} \qquad -(16)$$

where β and S are the standard carbon-carbon resonance and overlap integrals, respectively.

(3) Wolfsberg-Helmholz Approximation {11}

Somewhat similar to the Mulliken approximation, the expression for $\beta_{\mu\nu}$ now takes the form

$$\beta_{\mu\nu} = k(U_{\mu\mu} + U_{\nu\nu})S_{\mu\nu} \qquad -(17)$$

Here $U_{\mu\mu}$ may be taken to be equal to $-I_{\mu}$, and the Hinze and Jaffe values given earlier can be used. Once again, a request for k to be input appears on the screen with a default to a value given by

$$k = -\frac{\beta}{S} \times \frac{1}{2I_c} \qquad -(18)$$

(4) Nishimoto-Forster Approximation, {12}

This method, which has been shown to work well, {13}, in combination with the Nishimoto-Mataga definition of $\gamma_{\mu\nu}$ outlined earlier, within a P-P-P type of SCF approximation, assumes the following relation for $\beta_{\mu\nu}$

$$\beta_{\mu\nu} = A_0 + A_1 P_{\mu\nu} \qquad (19)$$

where $P_{\mu\nu}$ is again the bond order, and A_0 and A_1 are given as

Bond	A_0(eV)					A_1(eV)
	n* = 1	2	3	4	5	
C-C	-2.04	-1.90	-1.84	-1.82	-1.81	-0.51
C-N	-2.24	-2.09	-2.02	-2.00	-1.98	-0.53
C-O	-2.44	-2.27	-2.20	-2.18	-2.17	-0.56

Table 4.3

All of the above procedures for specifying both $\gamma_{\mu\nu}$ and $\beta_{\mu\nu}$ are controlled by the FORTRAN subroutine SCFBG, which is called in each SCF iteration. The argument list of this subroutine includes identifiers IGPAR and IFPAR, relating to γ and β parameter definitions, respectively. Values are automatically assigned to these identifiers when the individual schemes are interactively selected from the appropriate menus, and these are then used to bring into effect the desired sections of SCFBG. When either identifier is set to zero, no calculations of the corresponding integrals are performed in the call to SCFBG. Thus, for example, when using the P-P-P approximations for $\gamma_{\mu\nu}$ and $\beta_{\mu\nu}$, both IGPAR and IFPAR are set to zero after the initial computation of the integrals, so that these remain intact throughout the remaining iterations. Some of the other parameter schemes, as indicated above, require modifications to be made, based on up-to-date solutions, at each iteration. This is achieved by locating SCFBG within the iteration cycle.

Several experimental computer runs with the parameter schemes outlined above have already been undertaken. Experience suggests that the interactive graphics system can provide an excellent means of examining the comparative performance of the different schemes in a variety of situations. However, since much more evidence than has been obtained so far is needed before any firm conclusions may be arrived at, the results of these preliminary investigations will not be presented here.

Individual modifications to $\gamma_{\mu\nu}$, $\beta_{\mu\nu}$ and Z_μ elements may be made, as described in the previous chapter, before proceeding to the SCF-CI calculations themselves.

4.2 Planning SCF Calculations

The SCF equations allow, in principle, independent variation of the two parameters ω_μ and $\gamma_{\mu\mu}$ at the μ-th atom. However, it may be shown, {14}, that the same solution is generated by any pair of modifications $(\delta\omega_\mu, \delta\gamma_{\mu\mu})$ and $(\delta\omega_\mu^*, \delta\gamma_{\mu\mu}^*)$ provided that

$$\delta\omega_\mu + \tfrac{1}{2}P_{\mu\mu}^* \, \delta\gamma_{\mu\mu} = \delta\omega_\mu^* + \tfrac{1}{2}P_{\mu\mu}^* \, \delta\gamma_{\mu\mu}^* \qquad -(20)$$

where the same element $P_{\mu\mu}^*$ appears on both sides of the equation.

In particular, if $\delta\gamma_{\mu\mu} = 0$, so that only the framework integral associated with atom μ is changed by $\delta\omega_\mu$

$$\delta\omega_\mu = \delta\omega_\mu^* + \tfrac{1}{2}P_{\mu\mu}^* \, \delta\gamma_{\mu\mu}^* \qquad -(21)$$

and all pairs of values $\delta\omega_\mu^i$, $\delta\gamma_{\mu\mu}^i$ generating the same solution can be deduced from

$$\delta\omega_\mu = \delta\omega_\mu^i + \tfrac{1}{2} P_{\mu\mu} \, \delta\gamma_{\mu\mu}^i \qquad -(22)$$

This means that only $\delta\omega_\mu$ need be modified, and for each ground state solution thus obtained, variations with respect to $\delta\omega^i_\mu$ for a given $\delta\gamma^i_{\mu\mu}$ may be economically deduced by making use of the transformation (22).

The transformation (22) has been built into the graphics system, and the solutions obtained in the following section have been arrived at using this procedure.

4.3 Ground State Computations - Aniline

Aniline is chosen to illustrate the capabilities of the graphics system when used for investigating analytical properties of SCF solutions. Aniline is of particular interest since it possesses an N atom (see figure 4.3) which donates two electrons to the π electron system, and the effective nuclear charge is $Z_7 = 2$. No uniform charge distribution ($q_\mu = 1$ at all atoms) can be obtained. Thus the properties are quite different from those found in alternant hydrocarbons and those derivatives in which each conjugated atom contributes exactly one π electron.

4.3.1 Parameter Values

In the SCF calculations which follow, $\omega_{\text{carbon}} \sim -11\text{eV}$ is taken as the zero of energy, and then

$$\delta\omega_N = \delta\omega_7 = -15 \qquad -(23)$$

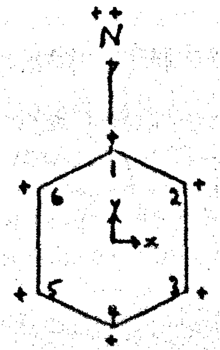


Fig. 4.3

is roughly the correct value required to give the value of ω_N quoted by Dewar and Paolini for N^{++}, {15}.

$$\gamma_{NN} = \gamma_{77} = 14.09 \qquad (24)$$

is the value of the electron repulsion integral given by Dewar and Paolini, and this will also be used here.

With these values as reference points, SCF solutions have been computed for six values of $\delta\omega_7$, ranging from -12.630 to -21.925. These have been stored and can be recalled by the user for analysis, or for calculation and analysis of derived quantities.

In the following sub-section, a step by step account is given of an experiment in the use of the graphics system to investigate the variation of charge density at each atomic centre with changes in the two parameters given by $\delta\omega_N = \delta\omega_7$ and $\delta\gamma_{NN} = \delta\gamma_{77}$. The aim is to produce, from the six stored solutions, plots of the charges q_r $(r = 7,1,2,3,4)$ as functions of ω_7 for given (constant) values of γ_{77}. From each of the six ground states, five curves, corresponding to $\gamma_{77} = 7.35, 11.35, 15.35, 19.35, 23.35$ are obtained from the transformation (22), thus demonstrating the economy in computational effort which the use of this transformation provides.

4.3.2 Application of the Graphics System

On loading the main program, the initial frame appears on the display screen

```
MOANAL ENTERED

1.  HEXAGONAL GRID
2.  CYCLIC SYSTEM
3.  OTHER MOLECULE
4.  LIBRARY LIST
5.  EXIT OR STORE
```

Fig. 4.4

Select menu item 4 by depressing console key number 4. The display now changes to -

```
MOANAL ENTERED





4.  LIBRARY LIST
```

Fig. 4.5

Point the light pen at 'CONTINUE' - displayed at the foot of the screen as shown in chapter three, but not included in these menu representations - to confirm the selection of item 4. (Each menu decision is confirmed in this way, but the action will not be mentioned henceforth in this description). Depress the foot-switch to activate the light pen and the program now branches to -

```
MOLECULES IN STORE

1.  BENZENE




5.  ANILINE
```

Fig. 4.6

Select item 5 to give -

```
ANILINE

1.  HUCKEL (10 SOLUTIONS)
2.  SCF (PPP) (6 SOLUTIONS)
```

Fig. 4.7

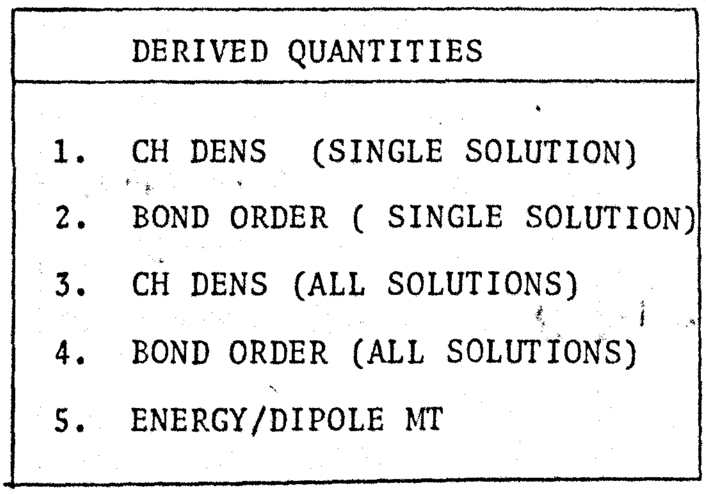
Select item 2 to give -

```
ANILINE

1.  F 7 7   -12.630
2.  F 7 7   -13.815
3.  F 7 7   -15.000
4.  F 7 7   -16.185
5.  F 7 7   -18.555
6.  F 7 7   -21.925
```

Fig. 4.8

No individual solution is to be examined at this stage. Charge density calculations are to be performed for all solutions in the set. Hence indicate 'CONTINUE', using the light pen. This leads to -

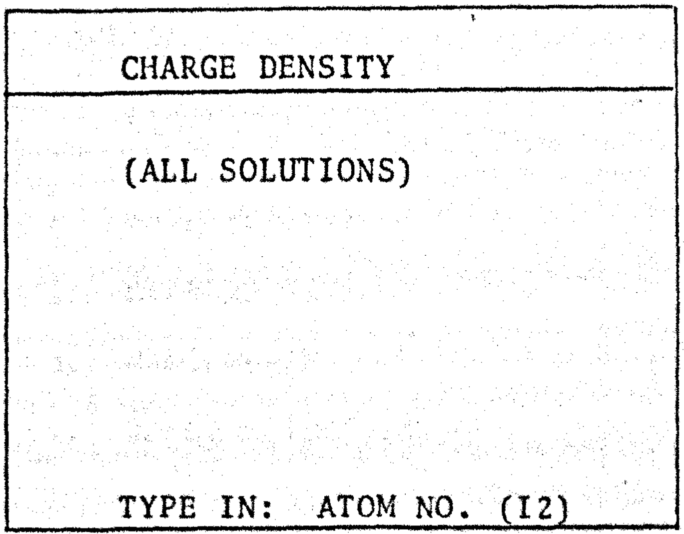


```
      DERIVED QUANTITIES

 1.   CH DENS  (SINGLE SOLUTION)
 2.   BOND ORDER ( SINGLE SOLUTION)
 3.   CH DENS (ALL SOLUTIONS)
 4.   BOND ORDER (ALL SOLUTIONS)
 5.   ENERGY/DIPOLE MT
```

Fig. 4.9

Only items 3 and 4 are applicable for calculations involving all solutions in the set. Selection of one of the other items would simply result in the menu of figure 4.9 being re-displayed. Therefore select item 3 to give -



```
      CHARGE DENSITY

      (ALL SOLUTIONS)




      TYPE IN:  ATOM NO. (I2)
```

Fig. 4.10

Type in 07.

The program now calculates q_7 for all six solutions in the set and creates a Y-array of q_7 values corresponding to an X-array of the $\delta\omega$ values which distinguish the solutions. The two arrays are carried forward automatically to the data analysis section -

```
PLOT ARRAYS

1.  TO PLOT
2.  STORE ARRAYS
3.  COLLECT ARRAYS
```

Fig. 4.11

It is desired to proceed to the plotting routines immediately, without storing the X and Y arrays. Hence select item 1. This results in the arrays being copied temporarily before the following display appears.

```
DISPLAY/MANIPULATION

1.  TO CURVE FIT
2.  DISPLAY DATA
3.  MANIPULATE
4.  RE-CONSTRUCT DATA
```

Fig. 4.12

Select item 1 to give -

CURVE FIT ROUTINES

1. LEAST SQUARE
2. POLYNOMIAL BUILD-UP
3. RETURN TO DATA

Fig. 4.13

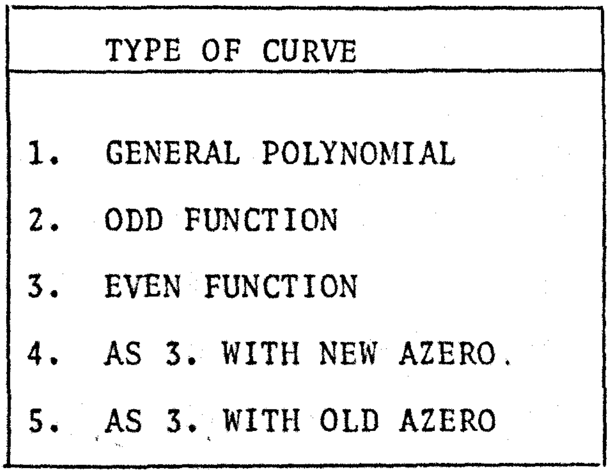
Select item 1 to enter the least square control routine. The first request is for the titles of the eventual graph, if required -

TITLES

1. NO TITLES
2. KEY, THEN TYPE TITLE
3. KEY, THEN TYPE X LABEL
4. KEY, THEN TYPE Y LABEL

Fig. 4.14

At this stage no titles are required, so select item 1, giving

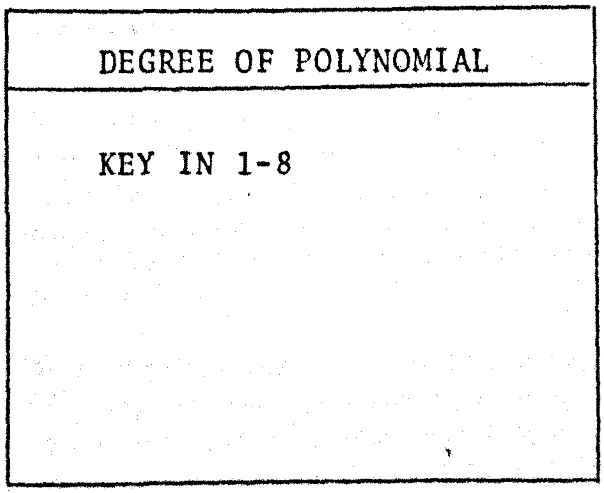


```
TYPE OF CURVE

1.  GENERAL POLYNOMIAL
2.  ODD FUNCTION
3.  EVEN FUNCTION
4.  AS 3. WITH NEW AZERO.
5.  AS 3. WITH OLD AZERO
```

Fig. 4.15

Select item 1, leading to



```
DEGREE OF POLYNOMIAL

KEY IN 1-8
```

Fig. 4.16

Key in 3 to give a cubic through the six data points (X_i,Y_i). The cubic equation and the curve itself are now displayed, but are not normally plotted at this stage. Depression of key 3 once again brings about a return to the display shown in figure 4.15. This enables a second curve to be drawn through the same data points for comparison, if required. However, at this stage 'CONTINUE' is selected, leading to -

```
CURVE OPTIONS

1.  TO DATA
2.  SAVE CURVE
3.  COLLECT CURVE
4.  COLLECT LAST CURVE
5.  TO CURVE FIT
```

Fig. 4.17

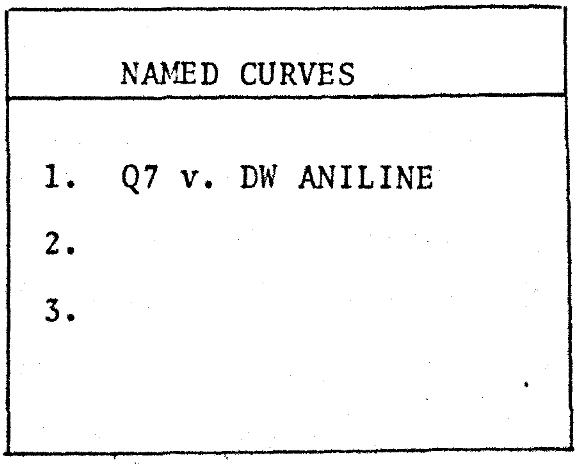
Select item 2 to store the curve in its polynomial coefficient form in a temporary buffer. This action brings up the display -

```
NAMED CURVES

1.
2.
3.
```

Fig. 4.18

Thus the curve can ge given a reference name which will be operative throughout the current run. The procedure is to indicate 'MODIFY' with the light pen, depress key 1, and finally type in the desired name. The result here is



NAMED CURVES

1. Q7 v. DW ANILINE
2.
3.

Fig. 4.19

Selection of 'RETURN' now brings about a return to the display shown in figure 3.17. From here it would be possible to return up the decision tree by means of a sequence of 'RETURN' requests, and to repeat the entire process from figure 4.8, first calculating and storing $q_1 v\delta\omega$, then again for $q_2 v\delta\omega$ etc., thus filling figure 4.19 with five names, each corresponding to a curve stored temporarily in polynomial coefficient form. However, since each curve must be transformed individually to produce a set of curves for given values of $\delta\gamma_{77}$, the procedure adopted is to first perform all the transformations and then plot the set derived from $q_7 v\delta\omega$, before returning to generate the other curves which are treated similarly.

Hence at figure 4.17, item 4 is selected to indicate that the next curve chosen will be the last of the current set (of one). This action brings up the display of figure 4.19 and the selection of item 1 now takes the curve $q_7 v\delta\omega$ forward to the transformation - and horizontal shift-routine section -

```
TRANSFORMATION/SHIFT

1.  KEY, THEN TYPE G
2.  KEY, THEN TYPE SHIFT
```

Fig. 4.20

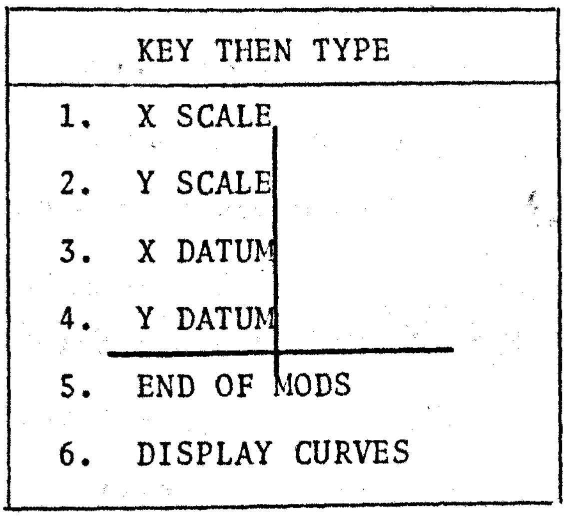
Select item 1, then type γ_{77} = 7.35. The non-linear transformation of the independent variable from $\delta\omega$ to $\delta\omega^{i}$, corresponding to $\delta\gamma_{77}^{i}$ = 7.35 -14.09, as given by (22) is now evaluated and retained. The transformed curve is named as a member of the set to be plotted -

```
PLOT SET

1.  Q7 v DWI, G77 7.35
2.
3.
```

Fig. 4.21

'RETURN' now takes control back to the display of figure 4.17, and the procedure from there is repeated for each transformation of the curve q_7 v$\delta\omega$ that is required. Eventually, the display shown in figure 4.21 contains all the five derived curves corresponding to γ_{77} = 7.35, 11,35, 15,35, 19,35 and 23.35. 'CONTINUE' now initiates a display of the numbered axes whose positions and scales have been computed automatically from the original data. Over-written are instructions indicating how to change the scales etc., to achieve better presentation and no loss of information with the combined display of curves.



KEY THEN TYPE

1. X SCALE
2. Y SCALE
3. X DATUM
4. Y DATUM
5. END OF MODS
6. DISPLAY CURVES

Fig. 4.22

The adjusted scales and axes may be examined (key 5) before the curves are displayed (key 6). At any time whilst the curves are being displayed on the screen, the action of typing 'P' on the console typewriter causes a hard copy plot to be made of the display by the graph plotter. The combined plot of transformed curves, as specified by the entire procedure above, is presented as graph number one in section 4.3.4. Alternatively, or after the plot has been completed, depression of key 1 takes control back to the display of figure 4.21, from which a further plot with revised scales etc, may be begun, or, by a sequence of 'RETURN' actions, the procedure may be recommenced at some earlier point.

In this current experiment, a return is made to the display shown in figure 4.8, and the entire procedure is repeated four times to produce the curves of q_1, q_2, q_3 and q_4, also given in section 4.3.4.

By a somewhat similar procedure, the dipole moment curve is generated from data points collected individually from the solutions. This too is subjected to the transformation, and the result is given as graph number six in section 4.3.4.

4.3.3 Comments on the Results

Some interesting conclusions may be drawn from an inspection of the curves produced.

(1) Charge Densities

It will be seen that as N becomes more electro-negative,

(a) $q_7 \rightarrow 2$

(b) q_i $(i \neq 2) \rightarrow 1$, although q_1 shows a peculiar turning point, due to the close proximity of the N atom which attracts negative charge, mainly from atom 1.

There is a "saturating" effect such that, as the charges approach the limiting values, large changes in electronegativity have a comparatively small effect on the charge distribution.

It would be possible to extend the range of parameter values to give, for example, a smaller electron charge density $q_N = q_7$, but such values would appear to produce unrealistic descriptions of the UV spectrum as will be described in the following chapter.

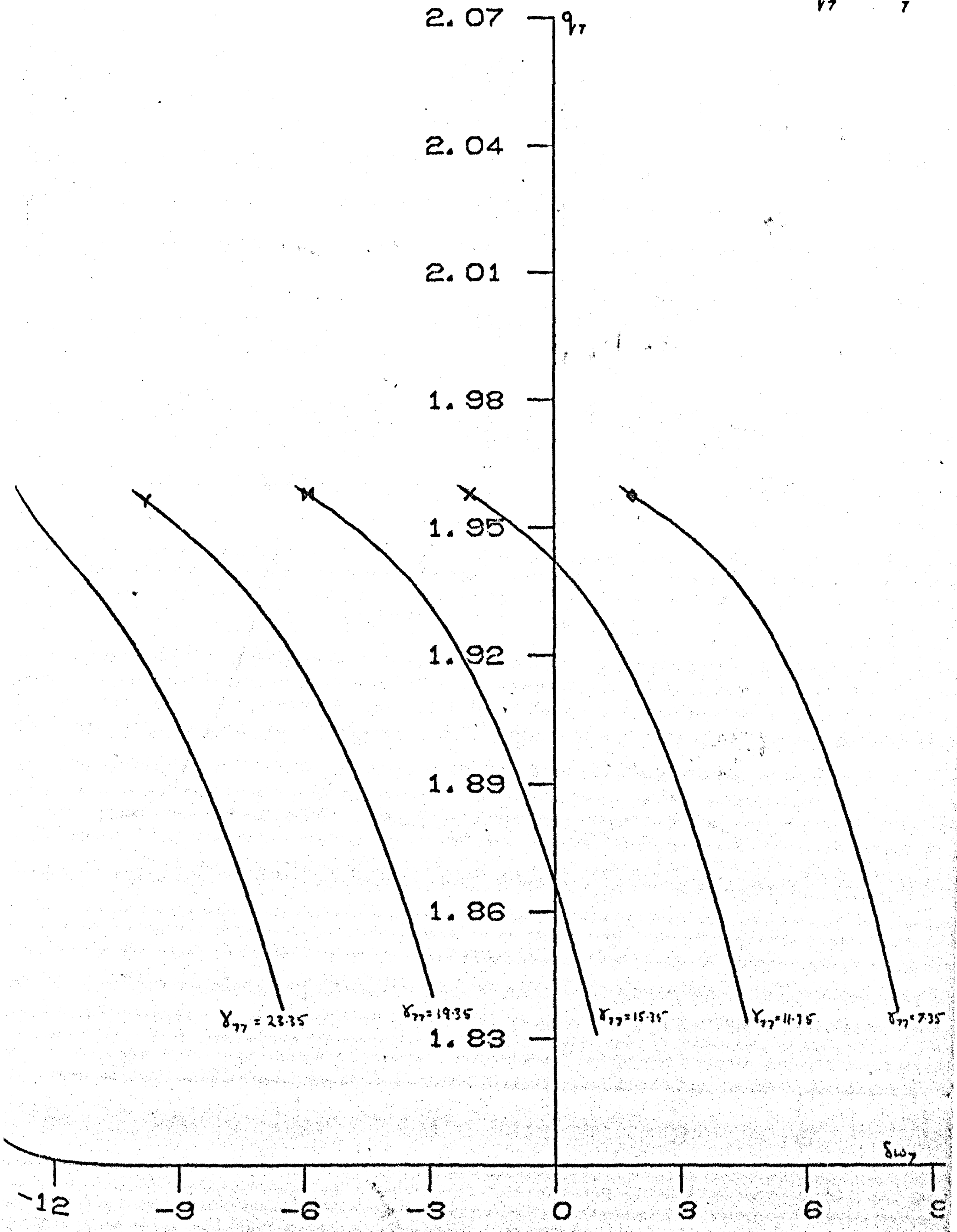
(2) Dipole Moment

The magnitude of the calculated dipole moment becomes larger with a shift in charge from N to the adjacent ring, i.e. it becomes smaller with increasing electronegativity at the N atom.

4.3.4 PLOTTED CURVES

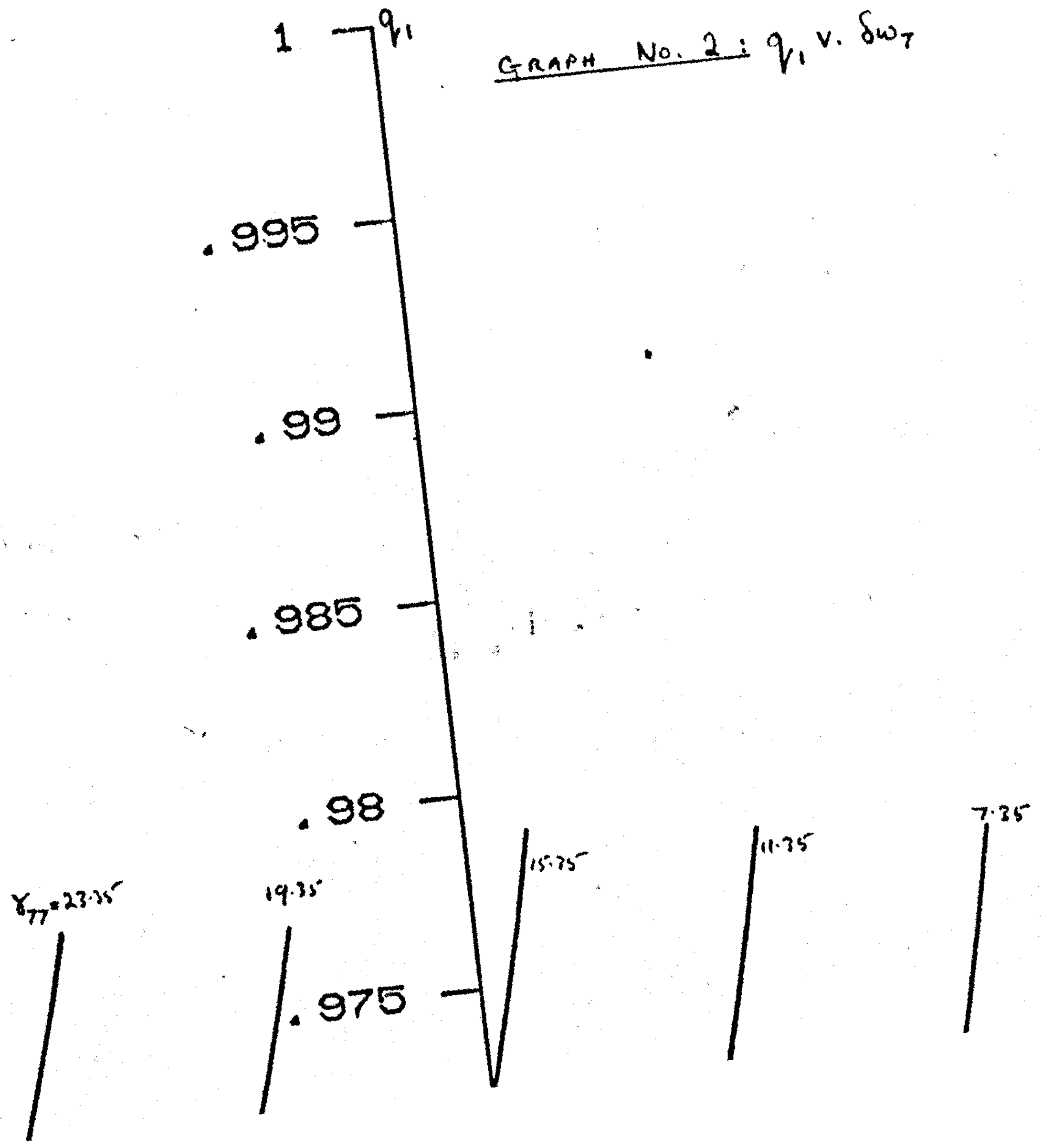
ANILINE

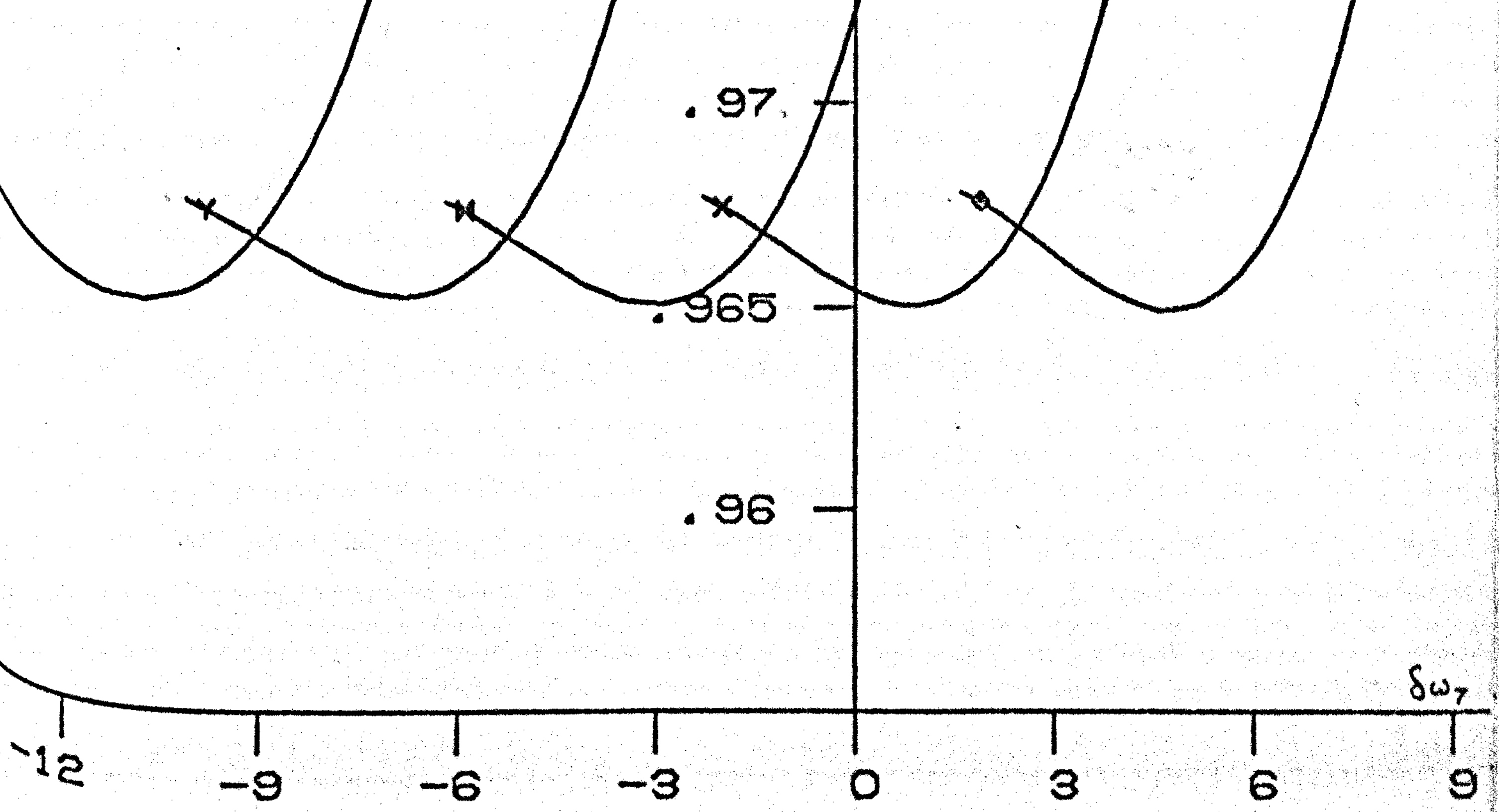
GRAPH NO. 1: q_7 v. $\delta\omega_7$



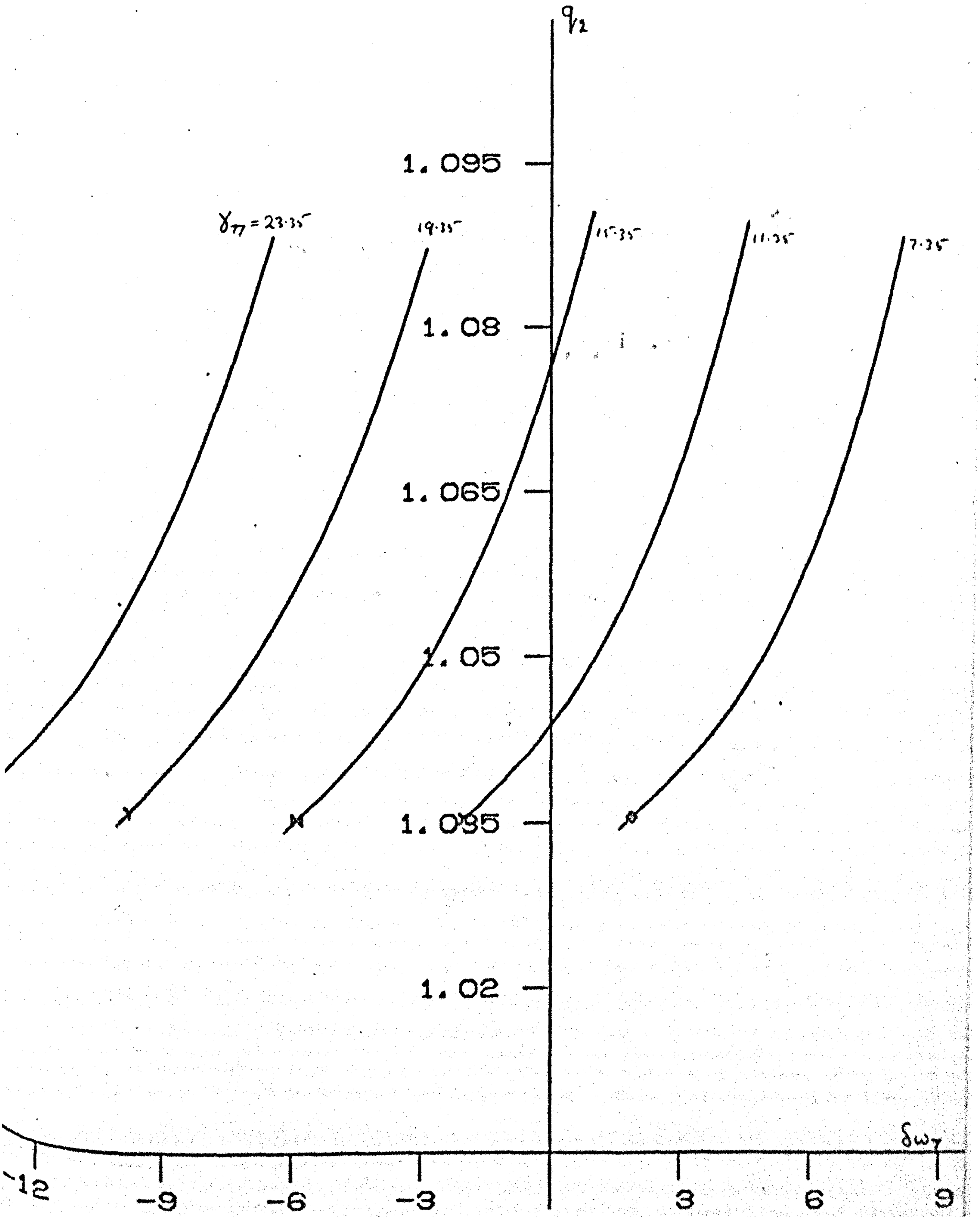
GRAPH NUMBER 1

GRAPH No. 2 : q_1 v. $\delta\omega_7$

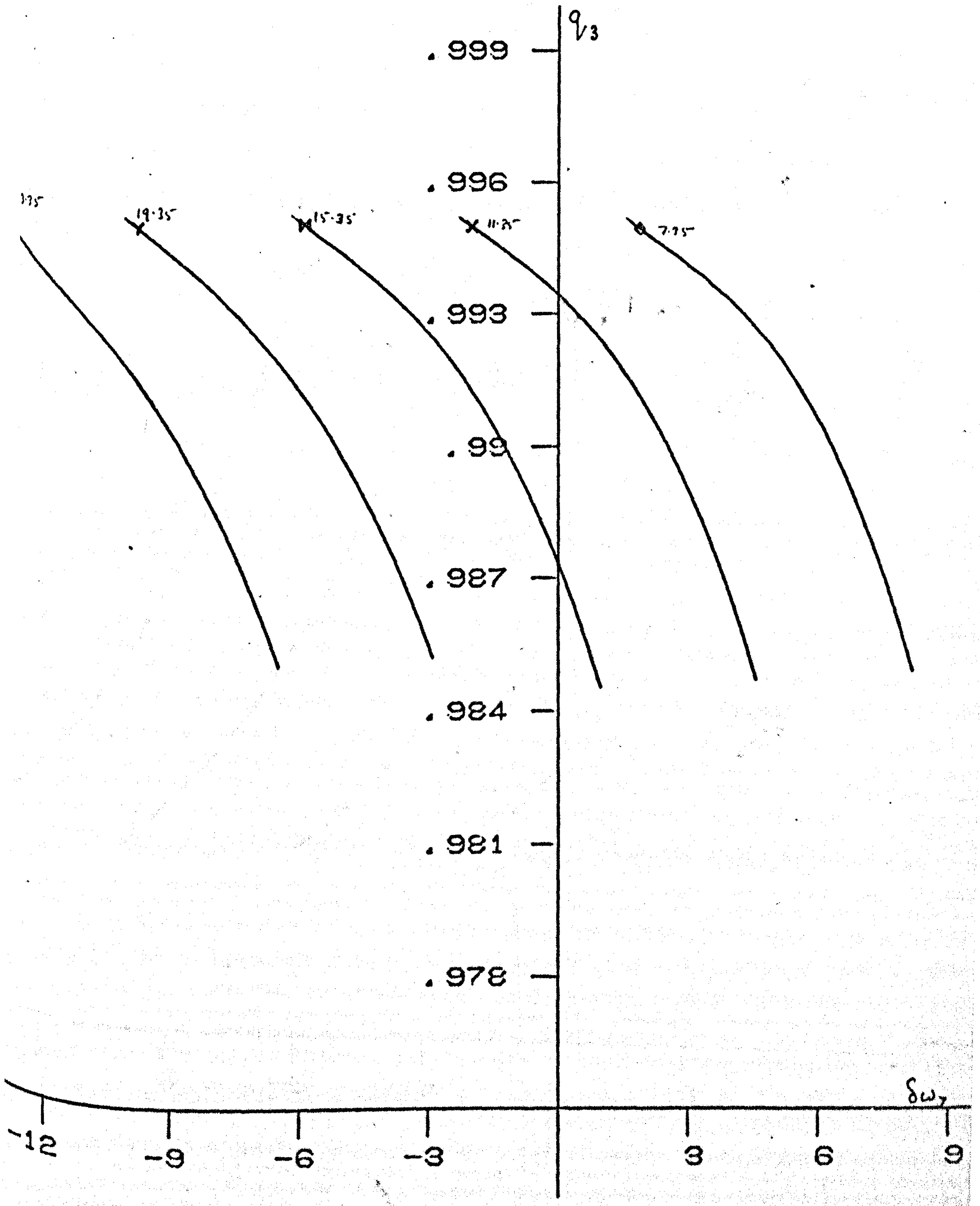



.97
.965
.96
$\delta\omega_7$
-12
-9
-6
-3
0
3
6
9

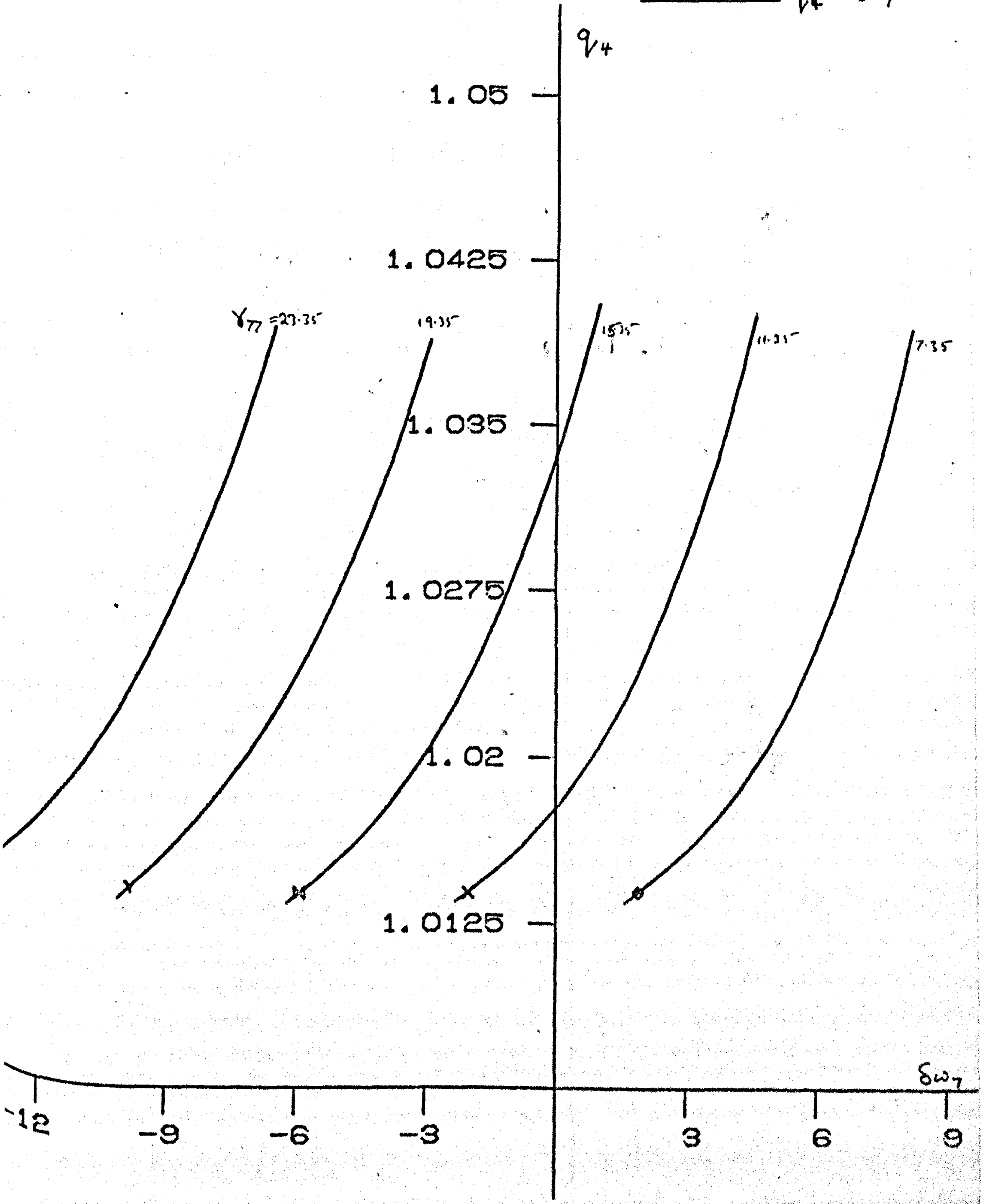
GRAPH No. 3: q_2 v. $\delta\omega_7$



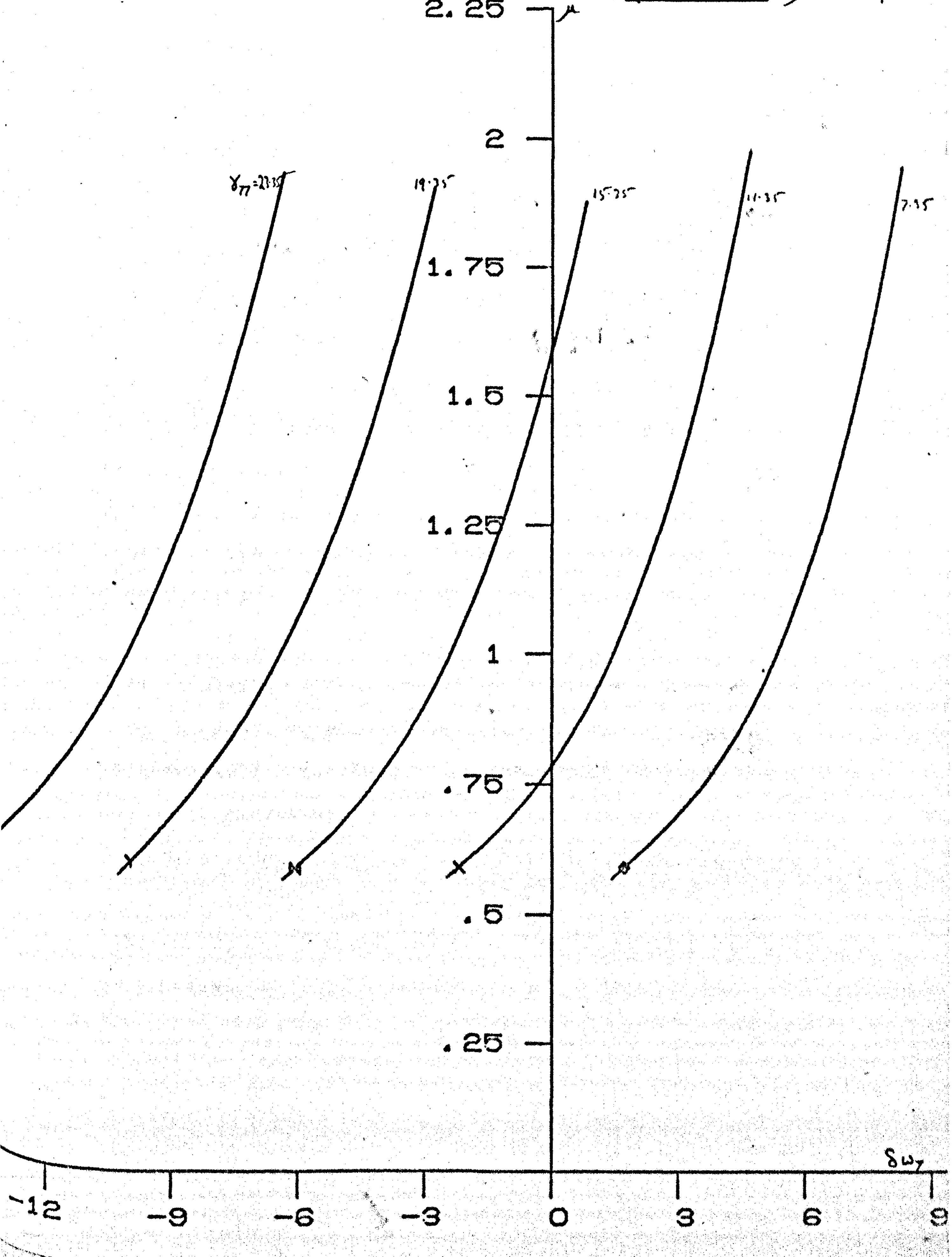
GRAPH No. 4: q_3 v. $\delta\omega_7$



GRAPH NO. 5: q_4 v. $\delta\omega_7$



GRAPH No. 6: μ v. $\delta\omega_7$



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CHAPTER FIVE

CONFIGURATION INTERACTION AND SPECTROSCOPIC PROPERTIES

This chapter demonstrates how the range of application of the graphics system extends beyond the ground-state analyses discussed so far, to the control of investigations into properties of spectroscopic states as described by CI methods.

An outline of the theoretical background to the CI method as it is applied here is first given. This is followed by brief details of the relevant computer programs and of their incorporation into the graphics system.

A discussion on the planning of SCF-CI calculations follows next. A basic procedure for the subsequently described experiments using the graphics system is established, and, as in the case of the ground-state calculations described in the previous chapter, it is seen that significant economies in computational effort can be made by careful planning and by the use of the transformation facility provided in the system.

Two applications are described. In the first, solutions of the CI problem for naphthalene are examined. Using this problem as an example, attention is focussed on some of the difficulties, which must be recognised and overcome, when using graphical computing techniques in this type of work. In particular, these are the questions of suitable scaling, satisfactory curve fitting, and accurate plotting of intensities when degeneracies arise or, similarly, of energies when the energy curves cross over.

The second application continues the work begun on aniline in the previous chapter, extending the investigation to the display and analysis of the results of CI calculations for this molecule.

Finally, the curves generated in both experiments are reproduced, in the form of plots taken directly from the graphical display, in a separate sub-section at the end of the chapter.

5.1 The Configuration Interaction Method

Transitions between ground states and excited states may be characterised by

(i) energies of excitation

and (ii) transition intensities.

An excited configuration results when a π-electron is transformed from an occupied orbital of the ground-state configuration to an unoccupied orbital.

In Huckel theory the energy of excitation $\Delta\varepsilon$ is given by

$$\Delta\varepsilon\ (i\rightarrow k') = \varepsilon_{k'} - \varepsilon_i \qquad -(1)$$

where ε_i is the energy of the doubly occupied orbital i in the ground state, and $\varepsilon_{k'}$ is the energy of the unoccupied orbital k'.

An expression for the oscillator strength, f, which is used to characterise the transition intensity, is

$$f = \frac{8\pi^2 mc}{3h}\ \bar{\nu}\ Q^2 \qquad -(2)$$

where c is the velocity of light

h is Planck's constant

$\bar{\nu}$ is wavenumber (cm^{-1})

and where

$$Q = \int \Psi_{exc}^{*} (\sum_{i} r_i) \, \Psi_0 d\tau \qquad -(3)$$

is the transition moment connecting the ground-state configuration Ψ_0 and the excited configuration Ψ_{exc}., the summation being taken over all π electron position vectors. The vector quantity Q has components Q_x, Q_y and Q_z, so that

$$Q = \sqrt{Q_x^2 + Q_y^2 + Q_z^2} \qquad -(4)$$

where, for example,

$$Q_x = \int \Psi_{exc}^{*} (\Sigma x_i) \, \Psi_0 d\tau \qquad -(5)$$

Hence Q is zero when $Q_x = Q_y = Q_z = 0$, thus defining a 'forbidden' transition of zero intensity.

The configuration interaction method describes a state S of a system of n π-electrons as a linear combination of configurations Ψ, each representing an assignment of the electrons to an available set of MO's, ψ, so that

$$S = \Sigma C_r \Psi_r \qquad -(6)$$

Singlet and triplet states of conjugated molecules can be approximated effectively by choosing appropriate configurations $\Psi(i \rightarrow k')$ corresponding to transfers of a π-electron from an occupied SCF MO ψ_i of the ground-state configuration Ψ_0 to an unoccupied SCF MO ψ_k'.

Thus

$$\Psi_0 = ||\psi_1(1)\psi_1(2)\ldots\psi_i(\mu)\psi_i(\mu+1)\ldots\psi_M(n-1)\psi_M(n)|| \qquad -(7)$$

represents the SCF ground-state configuration. Since the orbital replacement can be achieved in two ways, depending on spin assignments,

$$\Psi_{i\rightarrow k'} = \frac{1}{\sqrt{2}} \; ||\psi_1(1)\overline{\psi_1}(2)....\psi_i(\mu)\overline{\psi}_{k'}(\mu+1)...\psi_M(n-1)\overline{\psi_M}(n)||$$

$$- \; ||\psi_1(1)\overline{\psi_1}(2)...\psi_{k'}(\mu)\overline{\psi}_i(\mu H)...\psi_M(n-1)\overline{\psi_M}(n)|| \qquad -(8)$$

The π-electron states are determined by minimizing the total energy E with respect to variation of the Cr in (6). This is equivalent to solving the eigenvalue problem

$$hS = ES \qquad -(9)$$

where the elements of the CI matrix are given in the basis of configurations Ψ_r by

$$h_{IJ} = \int \Psi_I{}^* h_\pi \; \Psi_J \, d\tau \qquad -(10)$$

Elements connecting configurations $\Psi(i\rightarrow k')$ resulting from single replacements, and the ground state Ψ_0 are zero. Hence the eigenvalue problem is reduced by omitting Ψ_0 from (6), provided the lowest excited states are expressed as linear combinations of single orbital replacement configurations only.

E_0 the energy of the SCF ground state is adopted as the zero of energy by effectively subtracting it from the diagonal terms of the CI matrix, giving h_{II} in the form

$$\langle i\rightarrow k'|h_\pi|i\rightarrow k'\rangle = \Delta E_{ik'} \pm (ik'|k'i) \qquad -(11)$$

with

$$\Delta E_{ik'} = \varepsilon_{k'} - \varepsilon_i - [(ik'|ik') - (ik'|k'i)] \qquad -(12)$$

where +, - signs refer to singlet and triplet configurations, respectively.

It is interesting to compare (12) with (1), the corresponding expression in Huckel theory, which neglects contributions from electron-repulsion terms.

The off-diagonal elements of h are given by

$$<i\rightarrow k'|h_{\pi}|j\rightarrow \ell'> = -\left[(i\ell'|jk')-(i\ell'|k'j)\right] \pm (i\ell'|k'j) \qquad -(13)$$

where ε_i are SCF orbital energies and $(\lambda\mu|\nu\rho)$ are electron repulsion integrals expressed in terms of SCF MO's ψ_{λ}, ψ_{μ},... etc.

These integrals are obtained by a transformation from the given basis of atomic orbitals, that simplifies, in the overlap approximation, to

$$(ij|k\ell) = \Sigma c_{\mu i}c_{\mu j}c_{\nu k}c_{\nu \ell}\,\gamma_{\mu\nu} \qquad -(14)$$

where $\gamma_{\mu\nu}$ are electron-repulsion integrals referring to atomic orbitals ϕ_{μ}, ϕ_{ν}.

Since an excited state is described as a linear combination of single replacement configurations, component transition moments, calculated between Ψ_0 and Ψ_r $(i\rightarrow k')$ can be summed to give, for example,

$$Q_j^{x} = \int\Psi_0\, x\, (\Sigma_r C_{rj}\, \Psi_r(i\rightarrow k'))d\tau \qquad -(15)$$

which, by virtue of orthogonality between MO's, transforms to

$$Q_j^{x} = \sqrt{2}\, \Sigma_r C_{rj} \int\psi_{k'}x\psi_i d\tau \qquad -(16)$$

Oscillator strengths f_j for transitions from the ground state to excited singlet states S_j are then calculated from (2), where $\bar{\nu}_j$ are now transition energies (cm^{-1}) as computed by the CI method.

5.2 Program Details

The programs for calculating CI solutions within the interactive graphics system can be brought into operation as soon as a new SCF solution has been obtained and printed out.

At this point there is displayed the 'menu' -

```
      CI REPLACEMENTS.

 1.   CI NOT REQUIRED
 2.   AUTOMATIC - KEY,
      THEN TYPE LVLS (I2)
 3.   MANUAL - KEY, THEN
      TYPE TOTAL NO. (I2)
```

Fig. 5.1

If the first menu item is selected, the parameter LVLS is automatically set to zero and no CI computations take place, the SCF solution being carried forward alone for display or storage purposes.

LVLS may be given other values by first indicating item number two and then typing in the number. Normally used with the hexagonal grid device for specifying alternant hydrocarbons, the effect is to nominate automatically all possible single replacement configurations from the 2xLVLS innermost SCF MO's. This results in LVLSxLVLS replacement configurations $\Psi(i \rightarrow k')$ being selected, and hence determines the dimensions of the CI matrix. The subroutine SCFAG which handles this section of the overall procedure makes use of M, the number of occupied molecular orbitals and N, the number of atomic orbitals, both specified in the

SCF computation, and retained as part of the SCF solution.

The third menu item is selected when it is desired to nominate the replacement configurations individually. The procedure is to type in first the total number of replacements, and this initiates the display -

CI REPLACEMENTS

TYPE: OCCUPIED
THEN UNOCCUPIED (2I2)
MO NUMBERS

Fig. 5.2

The user then types in i and k' as instructed, until the total number of replacements specified has been input.

The elements of the CI matrix are now calculated as indicated by the expressions (11) and (13), and the diagonalisation process is undertaken. The resultant eigenvalues are the state energies E_j (in eV) relative to the SCF ground state, and the eigenvectors are the corresponding state wavefunctions S_j. Both the E_j and the S_j may be displayed in diagrammatic form, as described in chapter three. Oscillator strengths are also computed automatically, and these too may be selected by the user for display in spectra diagrams.

The CI solution, defined now as a vector of state energies, together with a vector of corresponding oscillator strengths and a note of the replacements used, plus any modifications to the present molecule, may be stored for later use. Sets of state energies or oscillator strengths can be built up by the user from stored solutions and may then be displayed collectively for comparison and for analytical purposes. Examples have already been shown in chapter three.

The SCF ground-state used for the CI calculation is retained temporarily, so that it is possible for the user to effect a return to the point in the program where modifications are specified (see figure 3.10), modify $\gamma_{\mu\mu}$ for example, and then initiate a new CI calculation, based on the same ground state configuration.

5.3 Planning SCF - CI Calculations

It was noted in the previous chapter that substantial economy in computational effort in respect of SCF ground state calculations could be made by varying just ω_μ of the two available parameters ω_μ and $\gamma_{\mu\mu}$ at the μ-th atom. Then, a transformation could be used to deduce the effects on derived quantities of variations $\delta\omega_\mu^i$ for a given $\delta\gamma_{\mu\mu}^i$. In many instances, further economy could be made by utilising properties of symmetry about $\delta\omega_\mu=0$, generating solutions on one side of the origin only, and then making use of the routine within the graphics system which generates appropriate image points.

A somewhat similar situation applies with the CI problem for alternant hydrocarbons. Here, a single SCF ground state configuration may be used with different values of $\gamma_{\mu\mu}$ to calculate several excited states, and transformations can then be made to the appropriate $\delta\omega_\mu{}^i$ axes corresponding to the given values $\gamma_{\mu\mu}$.

Suppose, for example, that the energy of the p band for naphthalene is to be plotted as a function of the varying $\delta\omega_\mu = \delta\omega_1$

(see figure 5.3) for the three values of

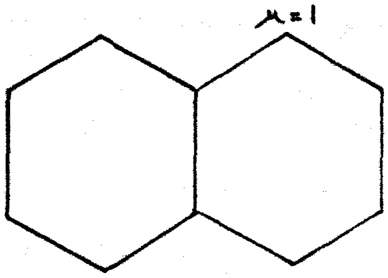


Fig. 5.3

γ_{11} shown in figure 5.4

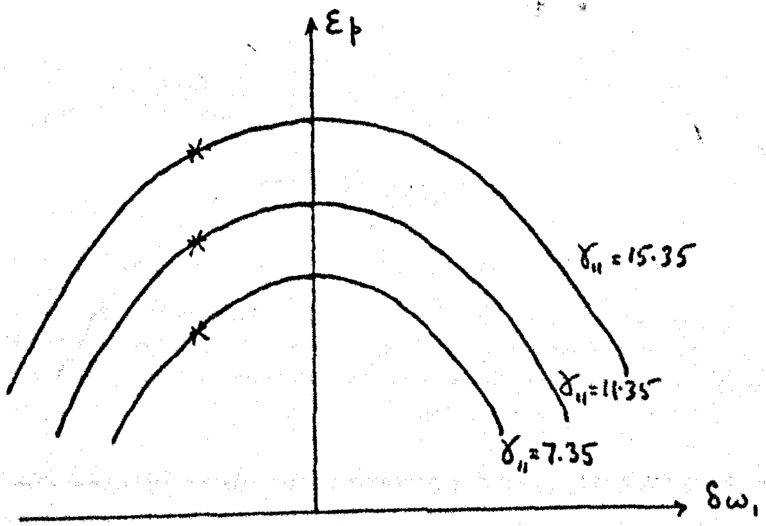


Fig. 5.4

In generating data points for these curves, three $\varepsilon_p{}^*$ values corresponding to a given value $\delta\omega_1^*$ can be found from a common SCF ground state with $\delta\omega_1 = \delta\omega_1^*$. This leads to a set of three curves, symmetrical about $\delta\omega_1=0$. Hence, it is only necessary to choose values of $\delta\omega_1$ on one side of the origin, and then, for each $\delta\omega_1$ to perform the SCF ground state calculation, followed by three CI calculations, resulting in considerable savings in computational effort.

The lowest and highest of the three curves, corresponding to $\delta\gamma_{11}^{i} = \pm 4$, may be "moved" from the symmetrical description of figure 5.4 to the "correct" positions relative to the associated γ_{11} values, as shown in figure 5.5, by means of the transformation

$$\delta\omega_1 = \delta\omega_1^{i} + \tfrac{1}{2}\, P_{11}\delta\gamma_{11}^{i} \qquad -(17)$$

The shifted curves are then symmetrical about $\tfrac{1}{2}\delta\gamma_{11}^{i}$. Thus further economy is provided by

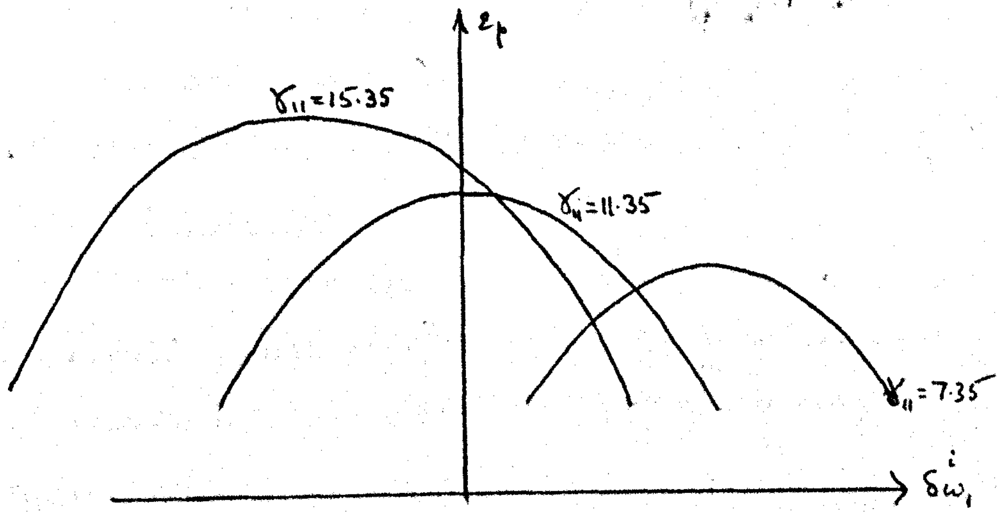


Fig. 5.5

all such curves being available from the symmetrical description by means of the transformation (17).

For the symmetric description it is possible to obtain Taylor expansion coefficients, for both energies and oscillator strengths. These are analagous to the perturbation coefficients of both Huckel and SCF ground-state theory, {1,2}. In principle these coefficients are available directly from the polynomial expression of the curves, as computed and displayed in applications of the interactive graphics system.

5.4 Experiments Using the Graphics System

In this section, the results from two separate experiments in using the graphics system to control investigations into the properties of excited states are presented and discussed. In the first experiment, which examines variations in the spectra of naphthalene derivatives, the capabilities of the interactive system are explored in such aspects of the problem as identifying and dealing with crossing energy levels, plotting intensities under the influence of degeneracies, and adjusting scales to give a more realistic representation of data.

The second experiment is concerned with the display and analysis of the results of CI calculations for aniline.

5.4.1 Naphthalene

In this experiment, seven SCF ground states, corresponding to modifications given by $\delta\omega_1 = 0, \pm\frac{\beta}{2}, \pm\beta$ and $\pm 2\beta$ at atom 1 as shown in figure 5.3, are computed using P-P-P parameters for $\gamma_{\mu\nu}$ and $\beta_{\mu\nu}$. For each of these, CI solutions consisting essentially of state energy vectors and associated oscillator strength vectors are obtained for $\gamma_{11} = 7.35$, 11,35, 15.35, 19.35 and 23.35. All possible single replacements are included in the calculations by setting LVLS equal to 5, but only the first ten components of each vector are in fact stored.

The experiment proceeds with the analysis of stored solutions by the interactive selection of appropriate vectors or single components, so as to build up data for both energy and intensity diagrams and curves.

5.4.1(a) Energy Curves

Graph 1 of sub-section 5.4.3 shows a combined plot of the state energies for $\delta\omega_1 = 2\beta$ to $\delta\omega_1 = -2\beta$, with $\gamma_{11} = 11.35$, i.e. $\delta\gamma_{11} = 0$, in every case. This is obtained by going to each of the ground states, picking out the second CI solution, and selecting an individual energy diagram, which is then passed forward as a member of the ultimately displayed set shown in graph 1.

The energy of the α band is plotted first. This is achieved by typing '01', resulting in the lowest state energy in each column being collected as a member of the Y array for the data analysis section of the program. The corresponding X array is automatically made up of the $\delta\omega_1$ values which distinguish the 'columns' of state energies.

Graph 2 gives the resultant curve, which is a quartic fitted by least squares, as are all the curves in this section.

By a similar process the energies of the p band (level 2) and the β' (level 7) can be plotted. These are given as graphs 3 and 4 respectively.

The β band for the unperturbed molecule ($\delta\omega_1 = 0$) corresponds to state energy level number five, (see graph 1). If '05' is typed, in an attempt to produce the E_5 curve by the same procedure adopted for the other bands, the resultant curve is that shown as graph 5. This is obviously an inferior fit through the displayed data points and suggests an inconsistent set of points.

In fact, the curves E_5 and E_6 cross over, and the data points must be chosen individually from the energy level diagram in graph 1. On bringing about a return to this display, the user types in any large two digit integer, other than '99', and this initiates the individual energy level selection routine. The message, "Type column no. and level no (2I2)" appears above the diagram. Then, using knowledge of the spectra (available here), or even by trial and error, the levels are nominated. In this case the correct input (see graph 1) is

```
0106
0206
0305
0405
0505
0606
0706
```

The resultant corrected curve for the β band is shown as graph 6.

The four energy curves are buffered and displayed collectively, for comparison in graph 7.

It is interesting to examine the complementary curve E_6 which crosses E_5. The straightforward selection of level '06' naturally produces incorrect data, resulting in the poor fit shown in graph 8. The "corrected" curve E_6 obtained by inputting

```
0105
0205
0306
0406
0506
0605
0705
```

is shown in graph 9. The curious shape of this curve is due to the data points possessing almost identical y-co-ordinates, resulting in a very fine vertical scale being adopted by the automatic scaling routines, thus exaggerating the effects of computational rounding errors. A more realistic representation of this curve is obtained by interactively adjusting the vertical scale (graph 10), and an even better picture is given by increasing the scale still further (graph 11).

It is possible to investigate how the energy curves vary with given values of γ_{11}. First of all, the curves for a single band are collected from diagrams such as graph 1 for each γ_{11} in the symmetrical description as described in section 5.3. Graph 12 shows E_1 v. $\delta\omega$ for all five γ_{11} values. It can be seen that in this case the curves are almost identical. The curves are now subjected to the transformation to give the more accurate description shown in graph 13. The corresponding curves for the p, β and β' bands are shown in graphs 14, 15 and 16.

In each case described above, the curve is a quartic, fitted by the least square method. The fits tend to be more accurate towards the centre of the range, there being a tendency to produce turning points near the range extremities. This effect is more pronounced in intensity plots, which are to be considered next. In practice the difficulty can be removed by increasing the number of data points in the region concerned, in which case the turning points are pushed further out from the origin, or by limiting the range of plotting. For the curves described in the following section, the latter course of action is taken, limiting the plots to a region extending from about $3\beta/2$ to $-3\beta/2$.

The problem has not been examined in great detail, partly because turning points will always arise with polynomial curve fitting, and the problem is initially one of determining an acceptable range on theoretical grounds. If a good fit over a wide range is required, then, almost certainly, spline fitting is to be preferred and this could easily be built into the graphics system. However, spline fitting does not provide the coefficients which can be related to 'perturbation' coefficients in the analytical sense. Polynomial fitting, in principle, provides these coefficients.

5.4.1(b) Intensity Curves

Curves of the oscillator strengths of the α, p, β and β' bands of naphthalene, with respect to variations of the core integral ω_1 and electron repulsion integral γ_{11}, may be produced from the stored solutions by a similar process to that already described for energies. The basic starting points, corresponding to the energy diagrams previously used, are now the spectra diagrams. From these, bands may be selected as before, and once again the β band requires special attention due to the effects of degeneracies.

Graph 18 shows the spectra for all seven $\delta\omega$ values with $\gamma_{11} = 11.35$, i.e. $\delta\gamma_{11} = 0$ in every case. The crossing of E_5 and E_6, mentioned earlier, can be clearly seen by tracing the intensity I_5 of the β band which, for the unperturbed molecule, is the largest of the three non-zero intensities.

For comparison, the corresponding diagrams with $\gamma_{11} = 7.35$, 15.35, 19.35 and 23.35 are given as graphs 17, 19, 20 and 21 respectively.

(i) α band

The α band intensity curves are extracted from each γ_{11} spectra diagram in turn by typing '01'. The combined symmetric curves are presented as graph 22. In this representation the five curves are virtually identical, showing zero intensity when $\delta\omega_1 = 0$. But, when transformed to the matching $\delta\omega_1^i$ axes, the curves for the individual γ_{11} values separate out, as shown in graph 23.

(ii) p band

The p band intensity curves are obtained by typing '02' at each spectra diagram. The combined symmetrical representation is shown in graph 24, with the transformed curves for the individual γ_{11} values given in graph 25. A notable feature of these graphs is the relative flatness of the curves for $\gamma_{11} = 23.35$.

(iii) β band

The β band intensity curves must each be obtained from the spectra diagrams by selecting levels individually in the manner described for energy curves. The combined symmetrical representation is shown in graph 26, and the transformed curves for each γ_{11} value are given in graph 27.

The β band shows virtually no variation in oscillator strength with change in electron repulsion integral γ_{11} at the modified atom, apart from a dramatic reduction around the origin when $\gamma_{11} = 23.35$. A change of this magnitude is an indication that the situation in this region should be examined more closely. In this case it is found that, as γ_{11} is varied towards the value in question, the β band begins to overlap a 'band', which has zero intensity in the unperturbed molecule. This may be seen by comparing graphs 18 and 21, and by an analysis of the numerical results which have been obtained for this case as follows ($\delta\omega$ = 0, throughout)

γ_{11}	7.35	11.35	15.35	19.35	23.35
E_4	5.717	5.717	5,797	5.928	6.009
E_5	6.021	6.021	6.021	6.021	6.026
I_4	0.0	0.0	0.002	0.022	0.775
I_5	2.192	2.191	2.187	2.168	1.418

Table 5.1

E_5 and I_5 tabulate the energy and intensity of the band, whereas E_4 and I_4 represent the neighbouring band, which at γ_{11} = 23.35 comes into close coincidence with the β band, and 'steals' roughly one third of its intensity.

Difficulties always arise in plotting intensities when degeneracies, or near degeneracies, occur, or similarly when energy curves cross, and these cases require careful analysis. Sometimes interactive graphics assists by highlighting anomolous situations of this kind.

(iv) β'_band

The β' band intensity curves are obtained by straightforward selection of level '07' from the spectra diagrams. Graphs 28 and 29 show the symmetrical and transformed curves, respectively.

The variation of intensity of the β' band due to a wide variation in γ_{11} in the modified atom is quite small by comparison with the change due to variation of ω_1. Unlike the β band, the β' band increases in intensity as ω_1 is changed from the standard value.

5.4.2 Aniline

It has been customary to seek an explanation of the UV spectrum of aniline on theoretical grounds by reference to the corresponding hydrocarbon, benzene. The spectrum of benzene has been described in terms of two forbidden low energy bands, α and p, which appear with low intensities, and two high intensity bands, β and β', which theoretically coincide, {3,4}.

In this section, a brief indication is given of the presentation on the graphical display of the results of CI calculations for aniline. The calculations are based on SCF ground states, obtained using the P-P-P approximation and parameter schemes, as described in the previous chapter. Twelve excitations

$$i = 1,2,3,4 \rightarrow k' = 5,6,7$$

as shown in figure 5.6, are specified interactively before each CI calculation.

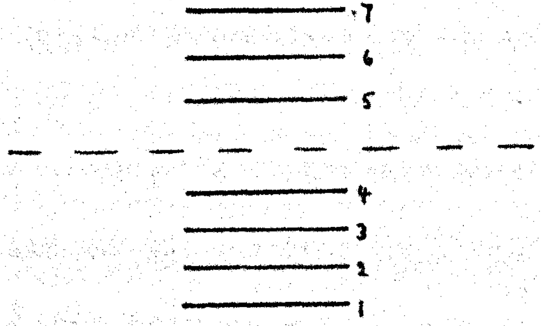


Fig. 5.6

The CI solutions, in the forms of state energy and oscillator strength vectors are named and stored as they are produced, and as with the analysis of the solutions for naphthalene, they are selected, by name, to build up the energy and spectra diagrams from which the curves are generated.

The choice of adjustable parameters has been restricted so as to produce results which appear to be plausible from comparison with experiment. However, this confines the study to a region in which the N atom retains a large π electron charge density, in the region of 1.8 and upwards, where the limiting value is 2. Within this region there was observed a 'saturation' effect, in which a large increase of electronegativity produces a comparatively small change in the charge distribution. A similar effect can be seen in regard to changes in the UV spectrum, where at large values of the electronegativity parameter associated with the N atom, the curves tail off asymptotically towards fixed values.

The discussion is limited to the β and β' bands, together with a higher energy band which, for convenience, can be referred to as the γ band.

In the limit as the N atom electronegativity is increased, the spectrum gives rise to two degenerate bands, analogous to those obtained for benzene, although the excitation energies do not coincide, due to the existence of exchange effects between the N atom and the ring.

The excitation energy of the β band is presented in graph 30 as a function of $\delta\omega_7^i$ for the five values 7.35, 11.35, 15.35, 19.35 and 23.35 of γ_{77}^i.

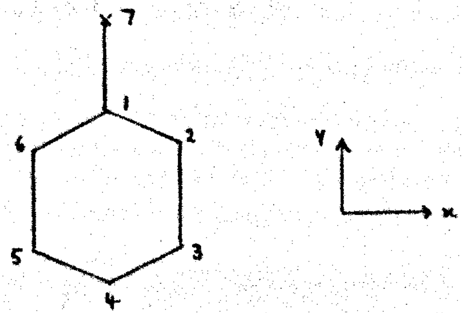
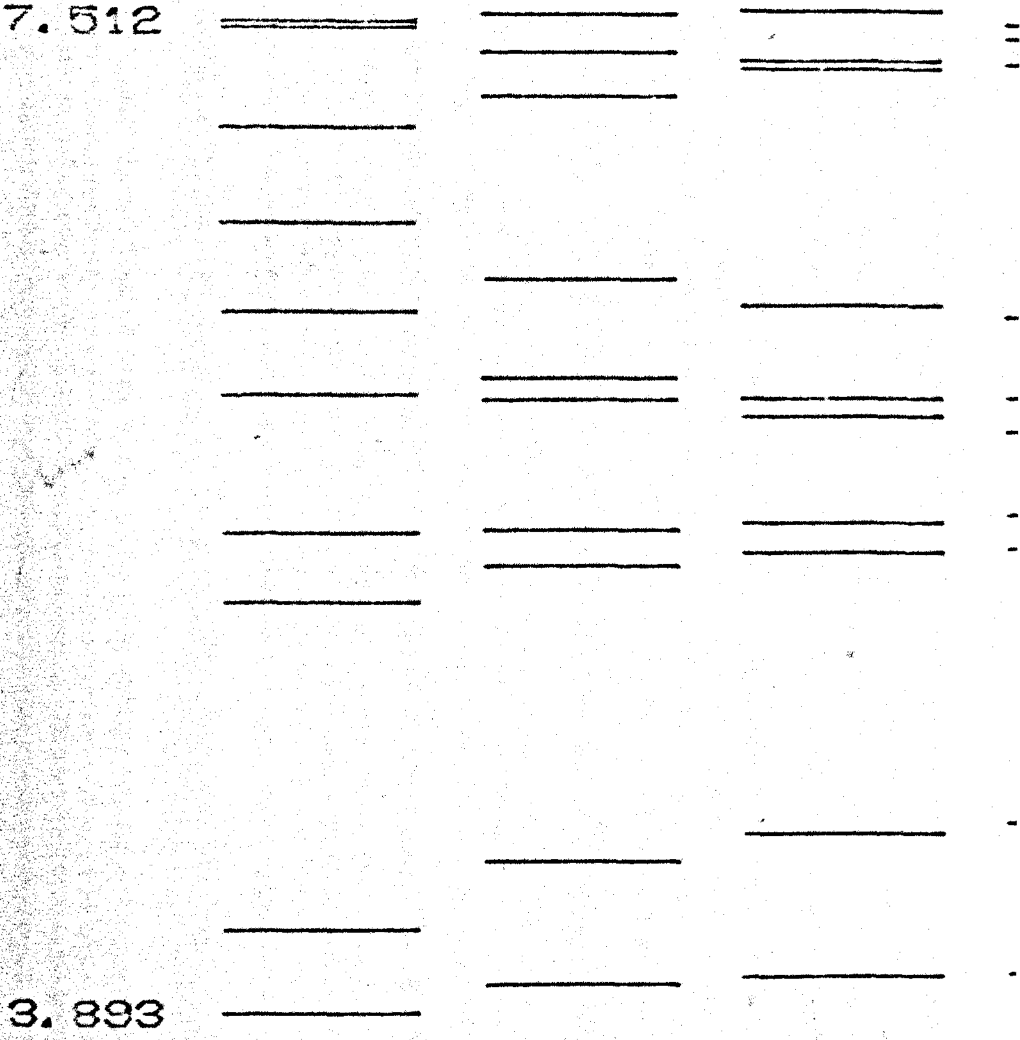


Fig. 5.7

The corresponding intensity curves for the β band are shown in graph 31. The intensity shows a tendency towards a value comparable to that obtained for benzene as the electronegativity is increased at the N atom. The polarisation of the band is along the short axis. The appreciable falling off in intensity as N becomes more electropositive is associated with a 'stealing' of intensity by the 'remote' γ band, whose excitation energy is plotted in graph 32 and intensity in graph 33. The falling away of intensity in the β band is associated with a large increase in intensity in the γ band. It is, however, important to confirm this interpretation by examining closely the weights of the configurations which contribute to the states describing the upper levels of the excitation process in both cases. Normally, in benzene the β band interacts with the α band, both having the same polarisation, but here the effect under discussion is almost entirely due to the γ band with the same polarisation.

The β' band is polarised in the direction of the long axis, and its excitation energy curves are represented in graph 34 with the corresponding intensity curves in graph 35.

There exists a γ' band of the same polarisation but of low intensity. As the N atom becomes increasingly electronegative the β and β' bands tend to coincide, as in benzene, and a similar property is observed in the γ and γ' bands which, in the limit, have zero valued oscillator strengths.



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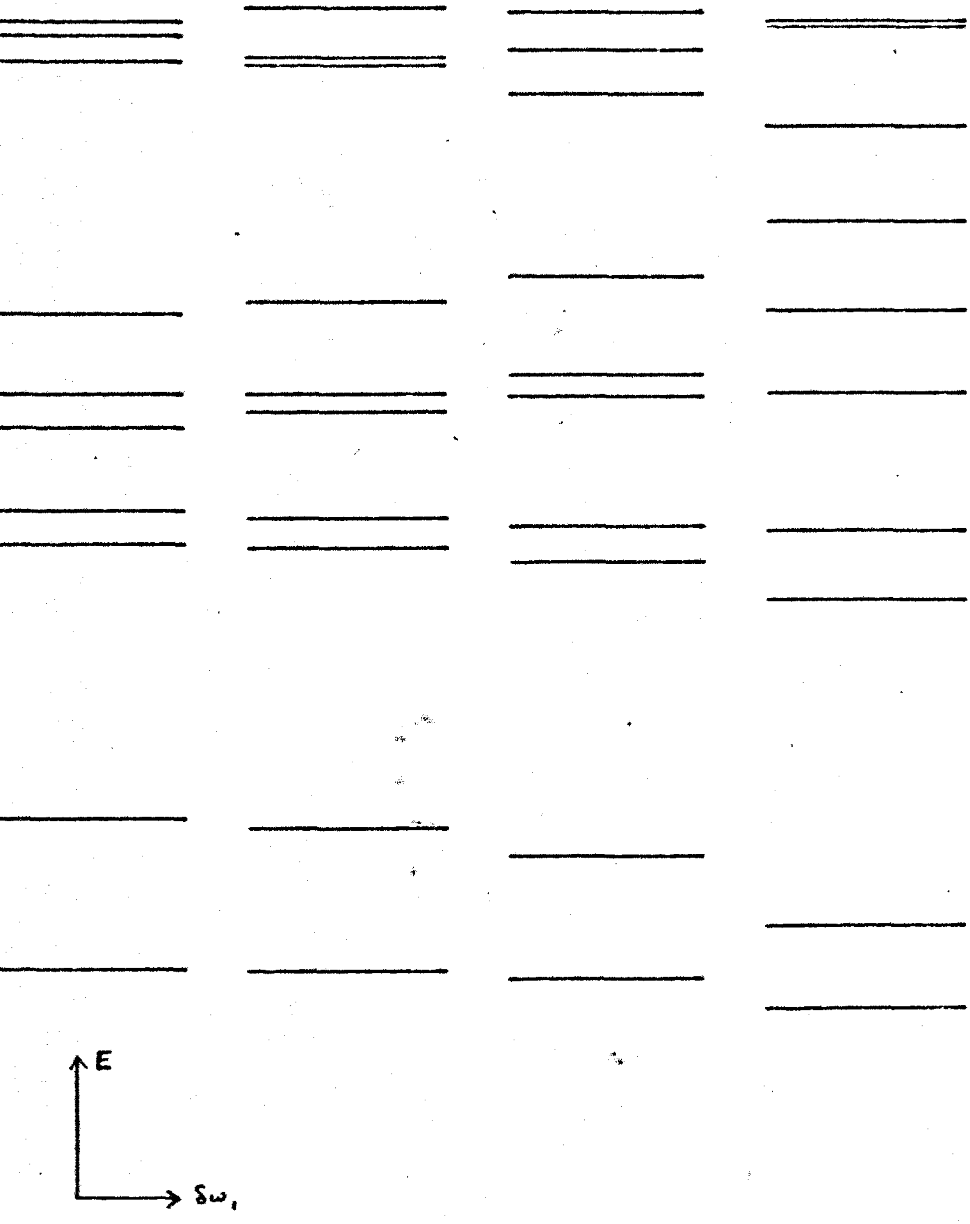
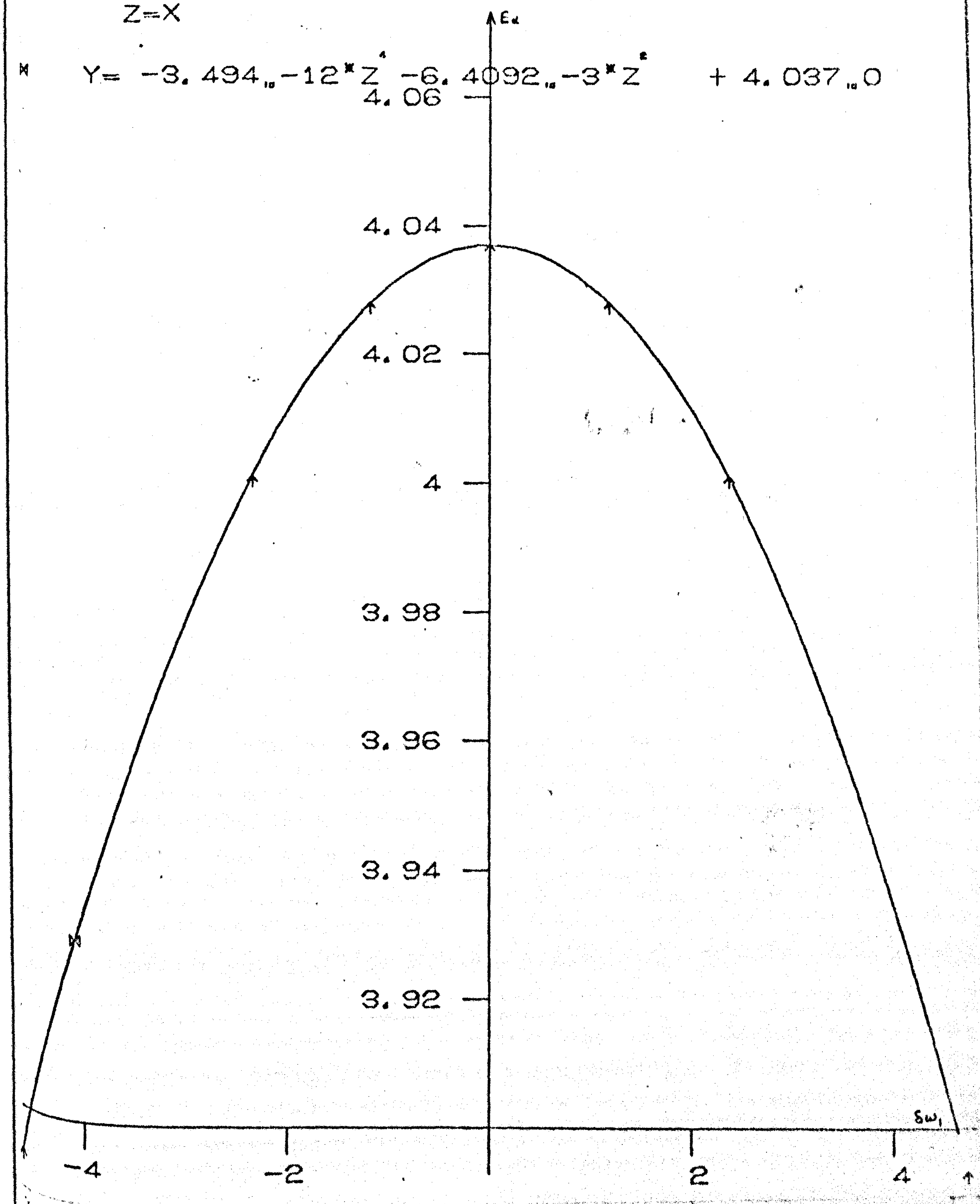
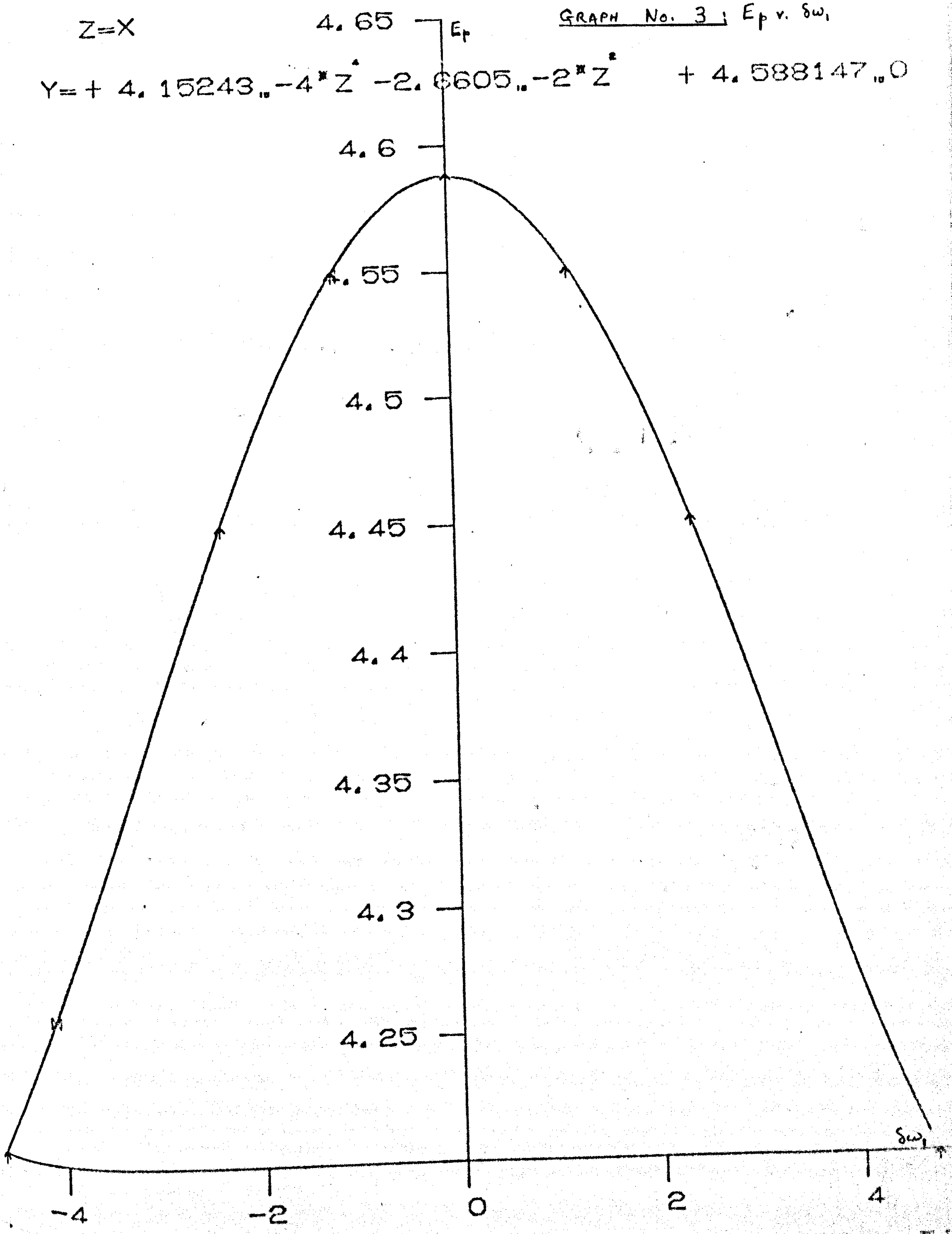
5.4.3 PLOTTED CURVES NAPHTHALENE GRAPH No. 1



LEVEL (I2) OR '00' FOR NO PLOT

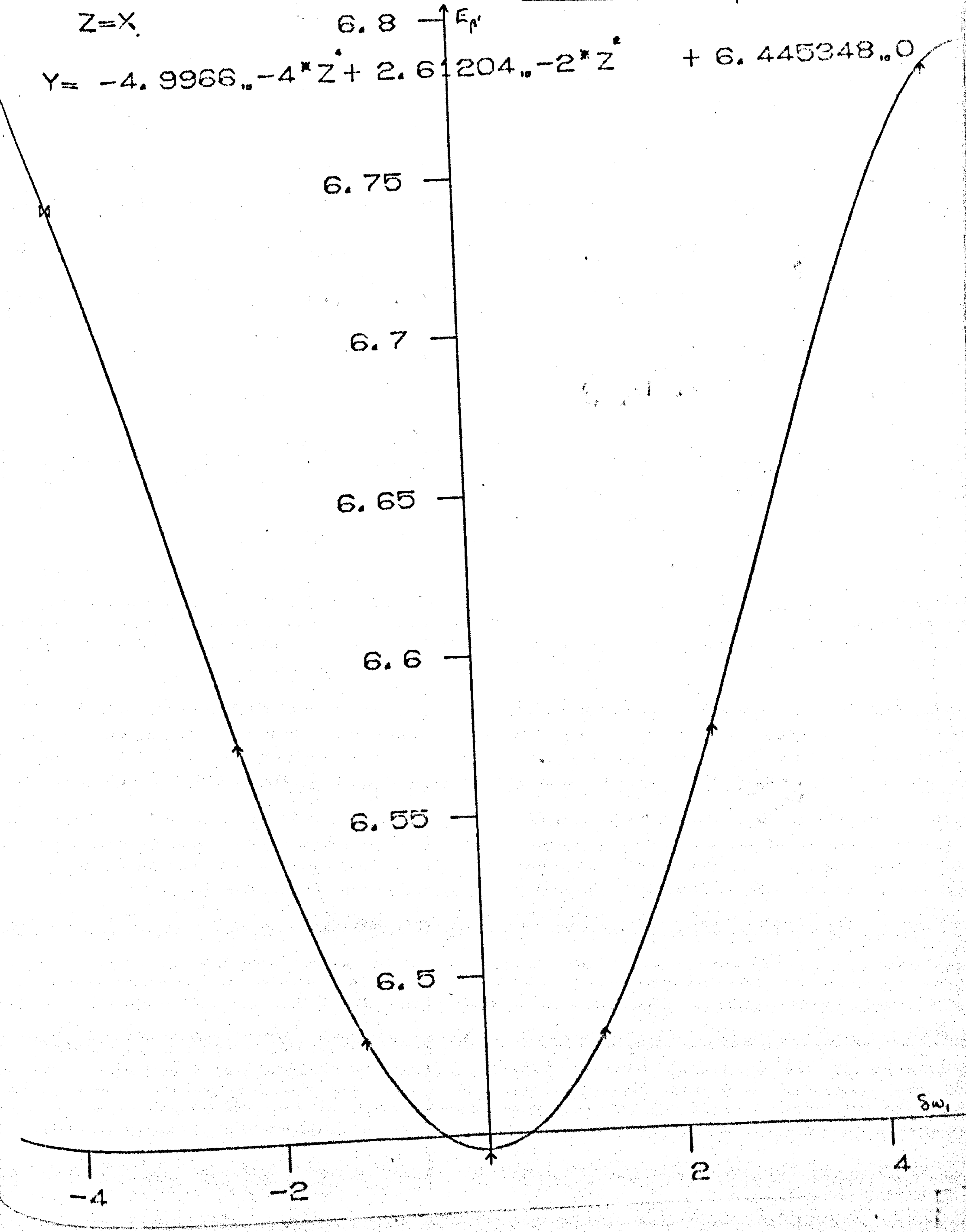
GRAPH No. 2 : E_α v. $\delta\omega_1$



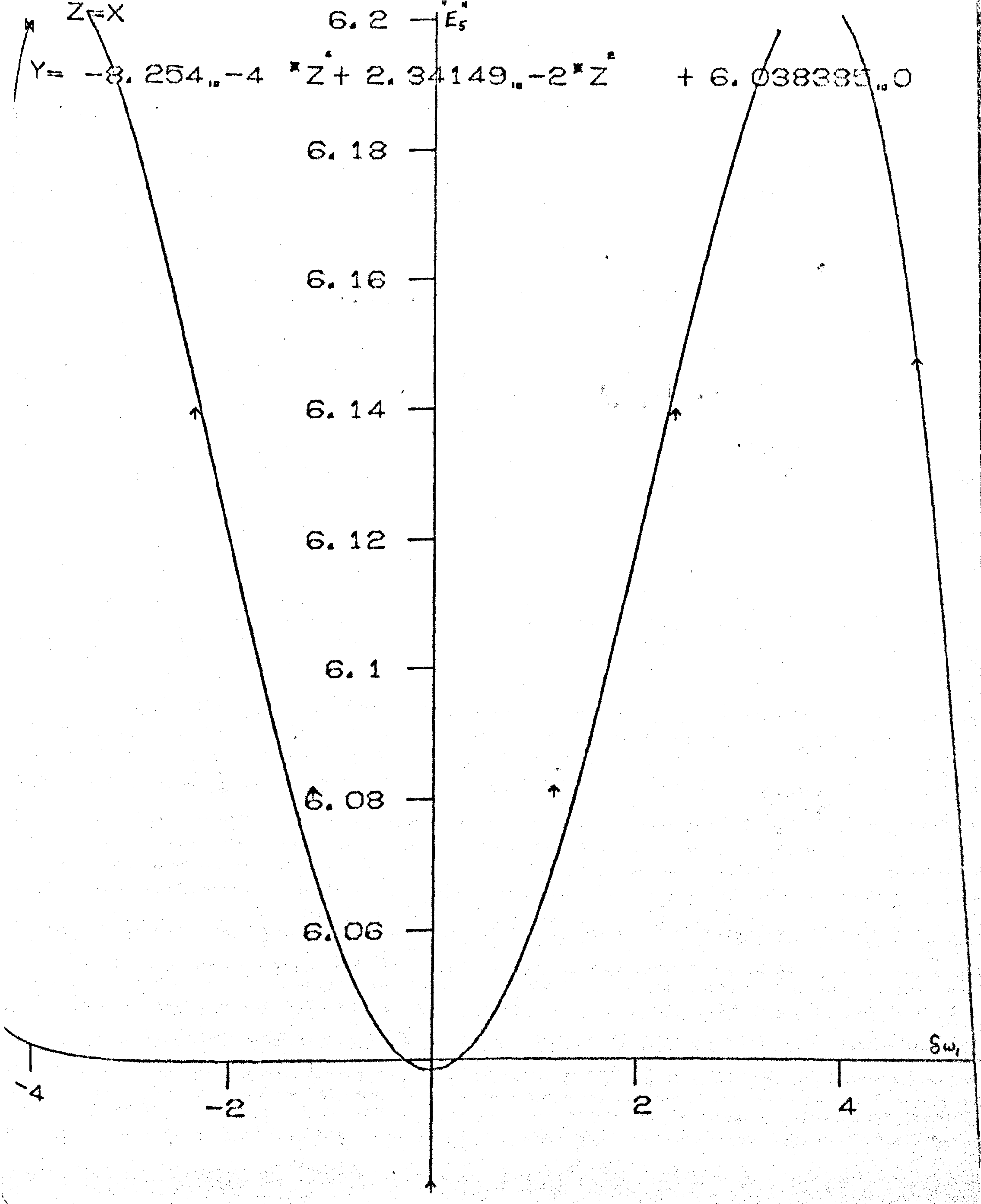


GRAPH No. 3: E_p v. $\delta\omega_1$

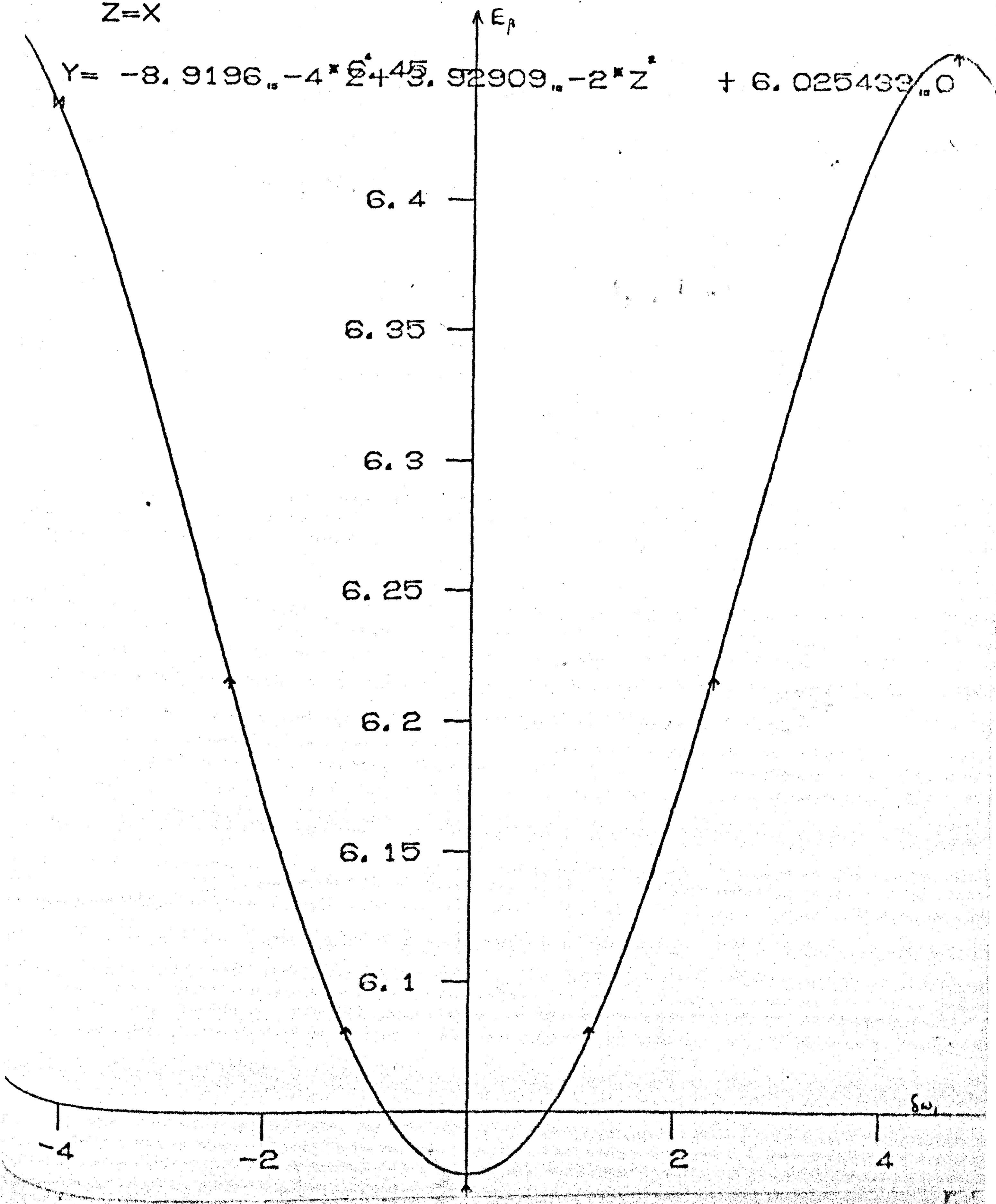
GRAPH No. 4 : $E_{\beta'}$ v. $\delta\omega_1$



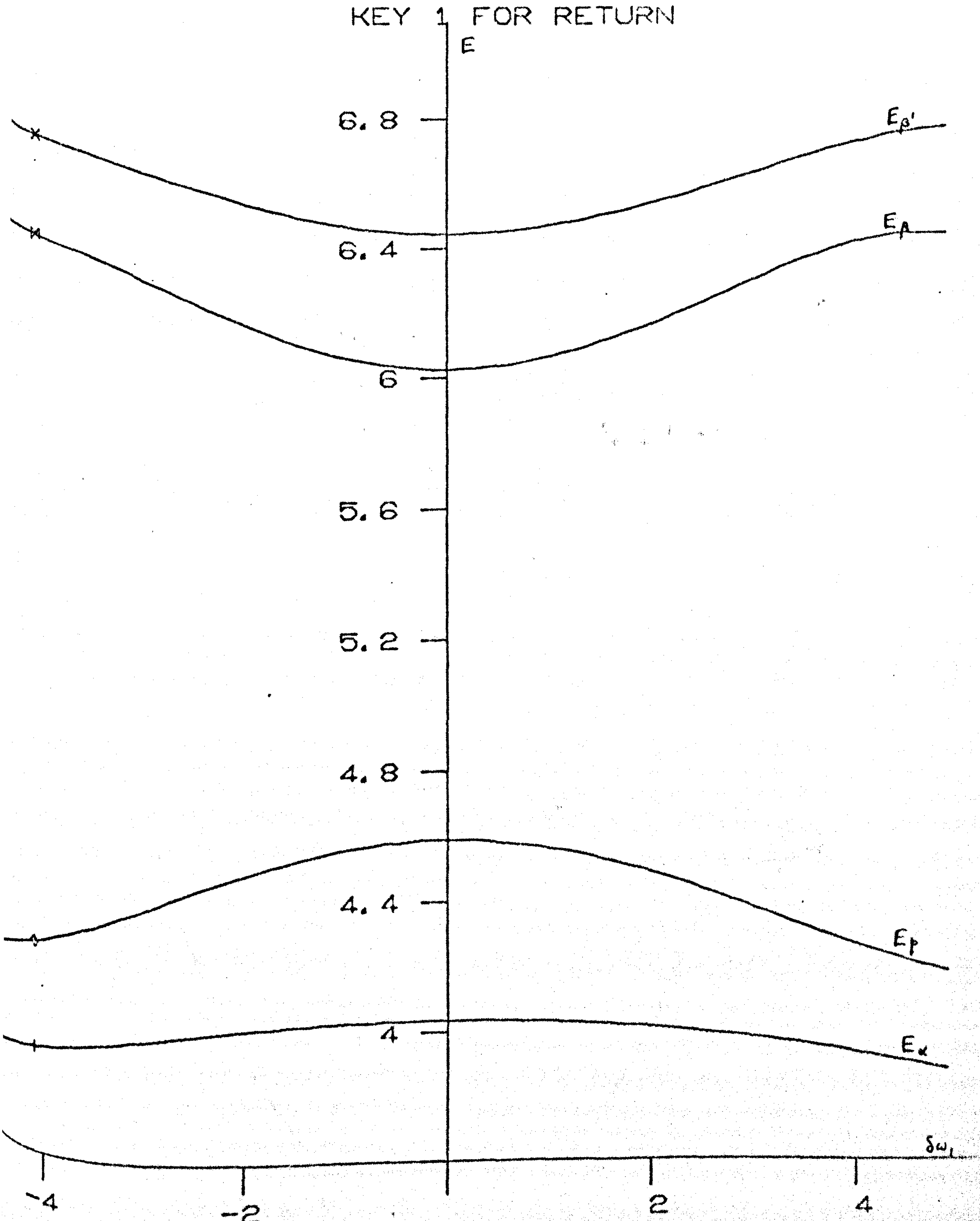
GRAPH No. 5 : "E_5" v. $\delta\omega_1$



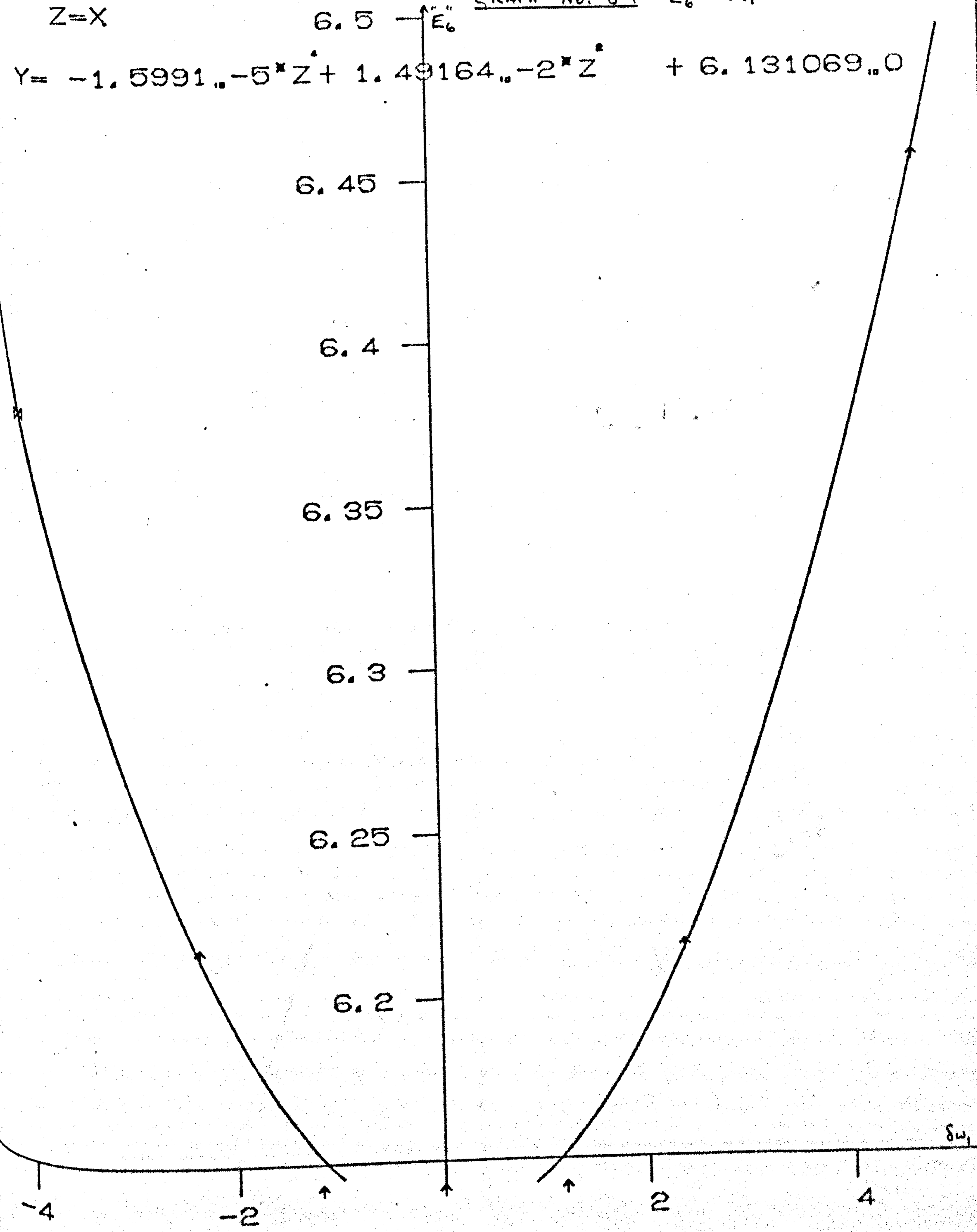
GRAPH No. 6: E_β v $\delta\omega_1$



GRAPH No. 7 : $E_\alpha, E_p, E_\beta, E_{\beta'}$ v $\delta\omega_1$



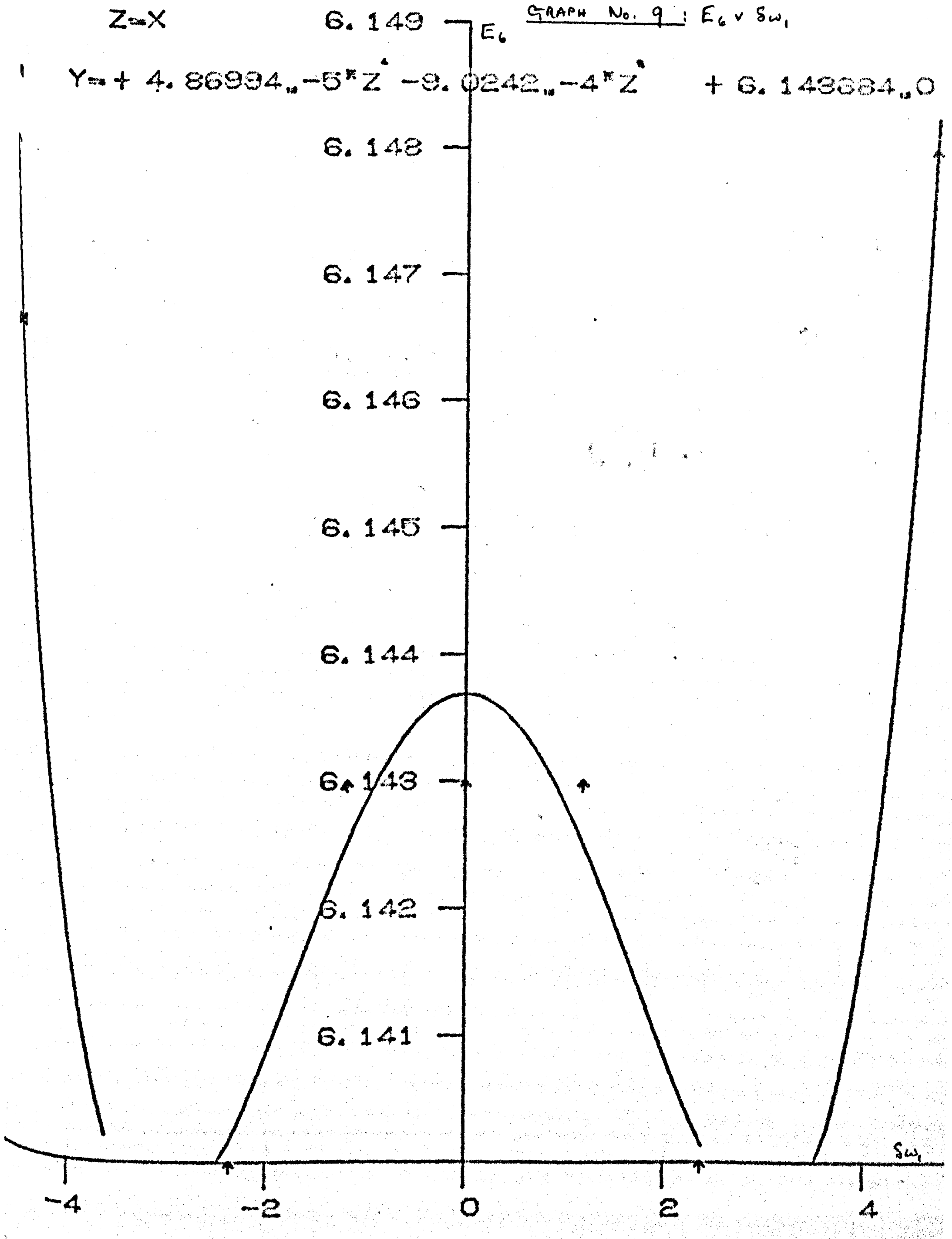
GRAPH No. 8 : "E_6" v $\delta\omega_1$



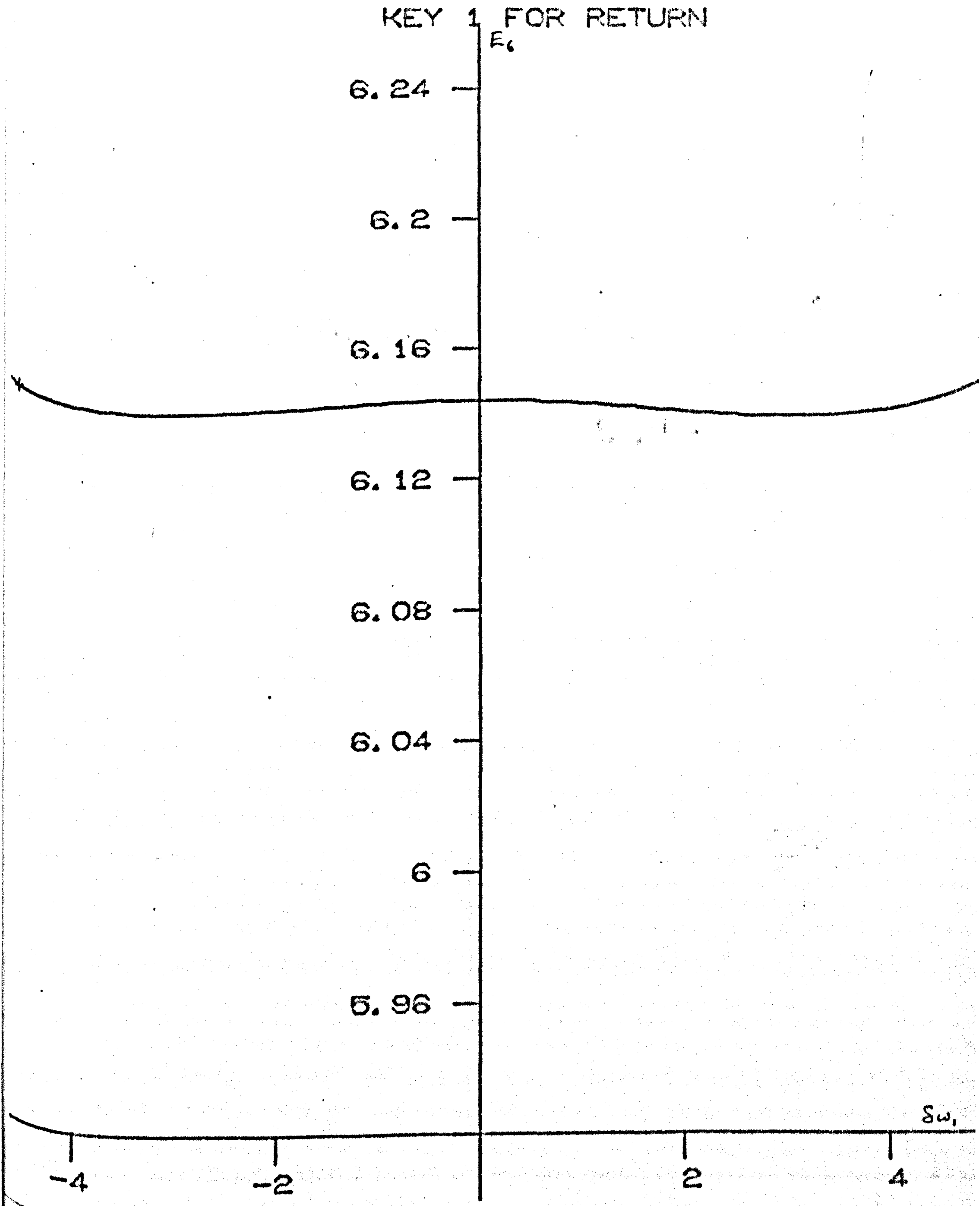
Z=X

$Y = -1.5991_{10}-5 * Z^4 + 1.49164_{10}-2 * Z^2 + 6.131069_{10}0$

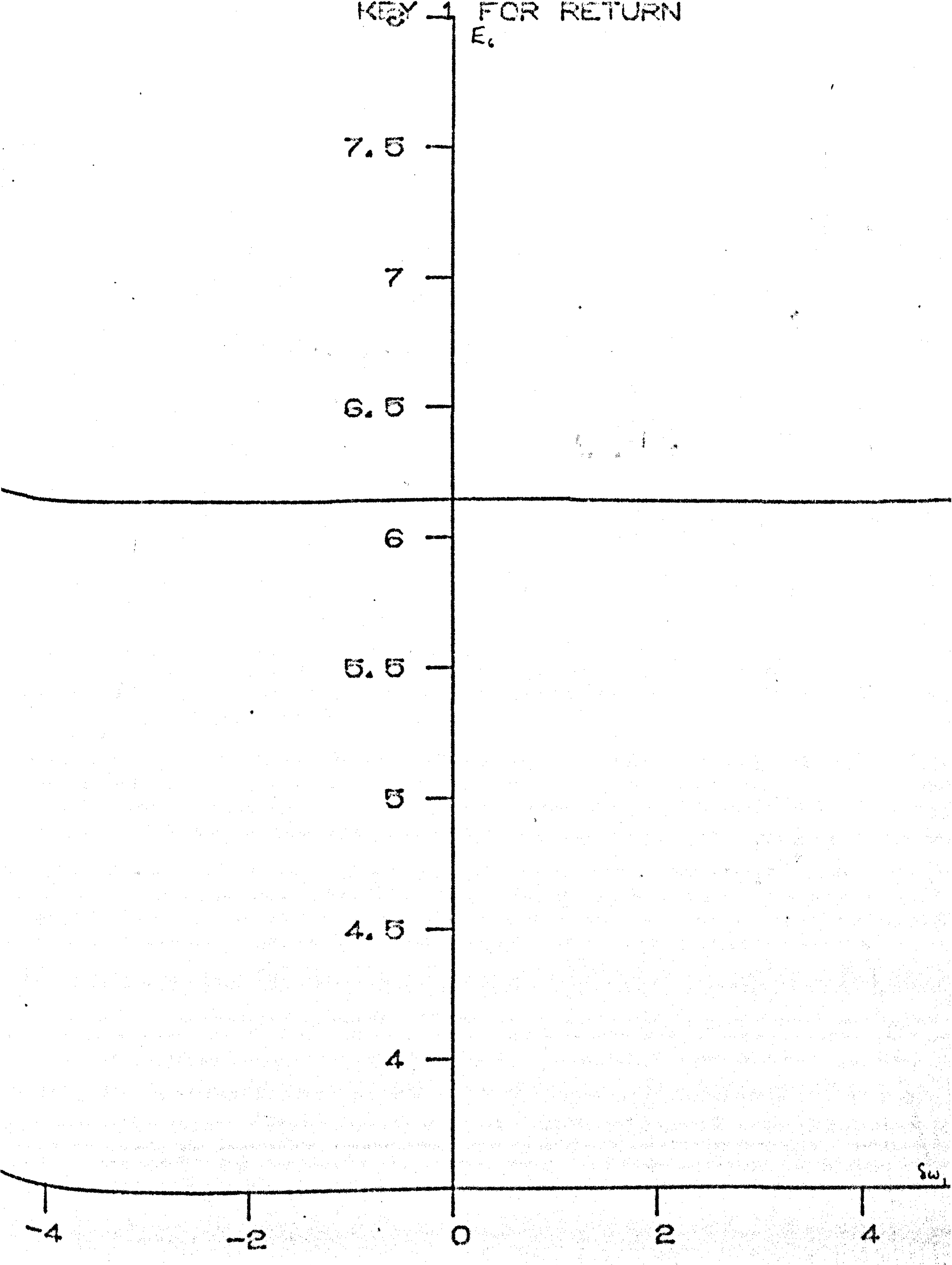
GRAPH No. 9 : E_6 v S_{ω_1}



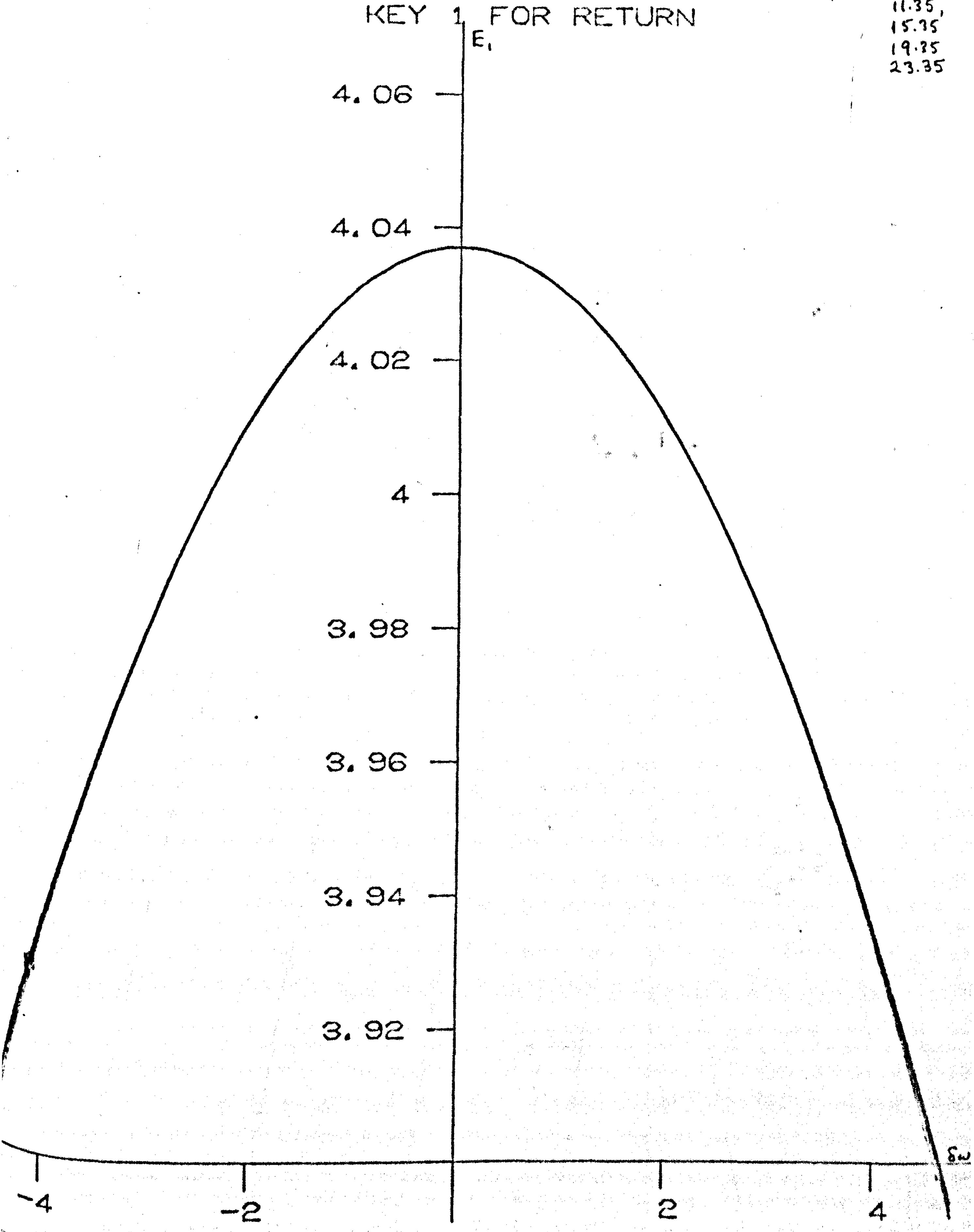
Graph No. 10 : E_6 v. $\delta\omega_1$



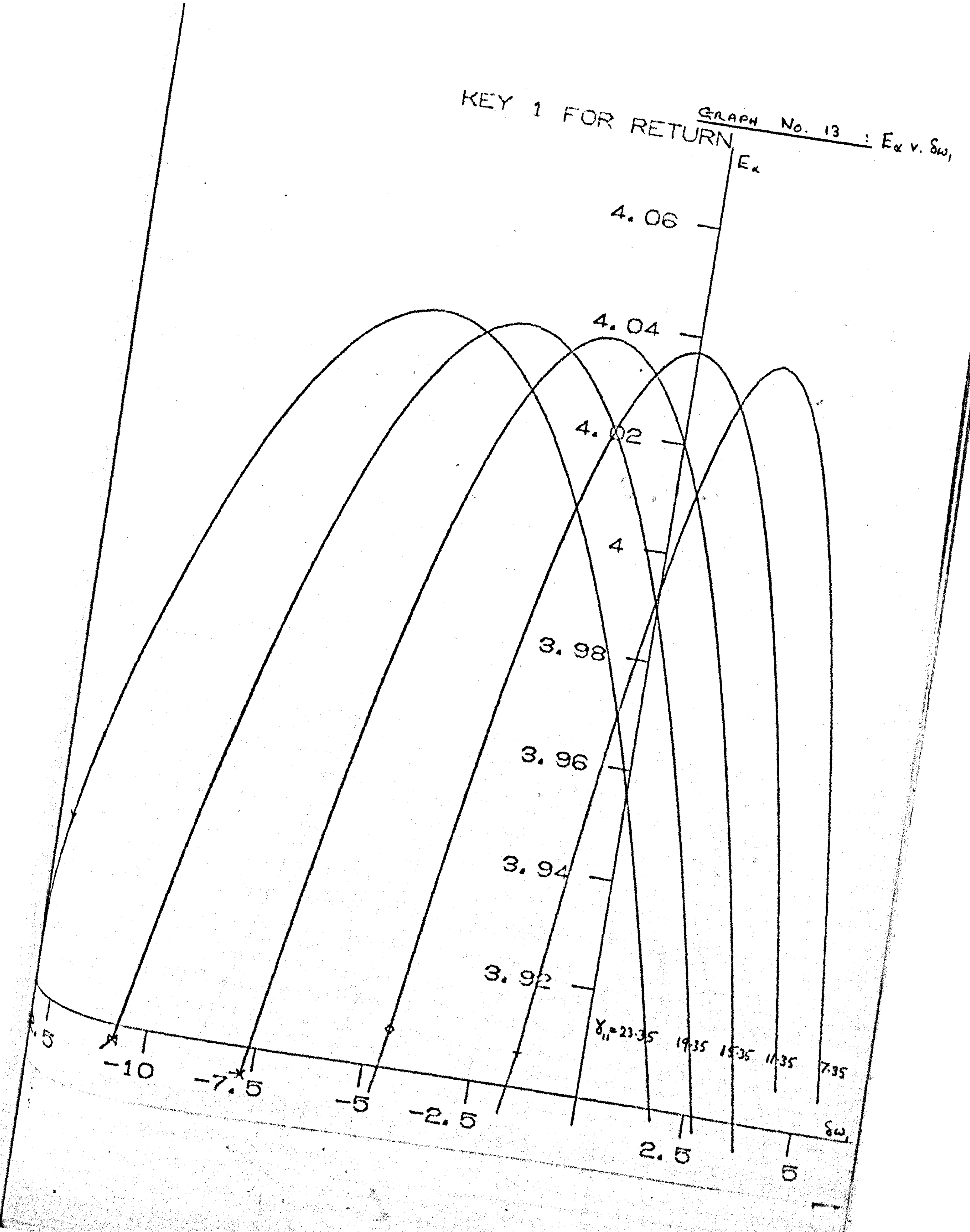
GRAPH No. 11 : E_6 v. $\delta\omega_1$



GRAPH No. 12: E_1 v. $\delta\omega_1$, γ_{11} = 7.35, 11.35, 15.35, 19.35, 23.35

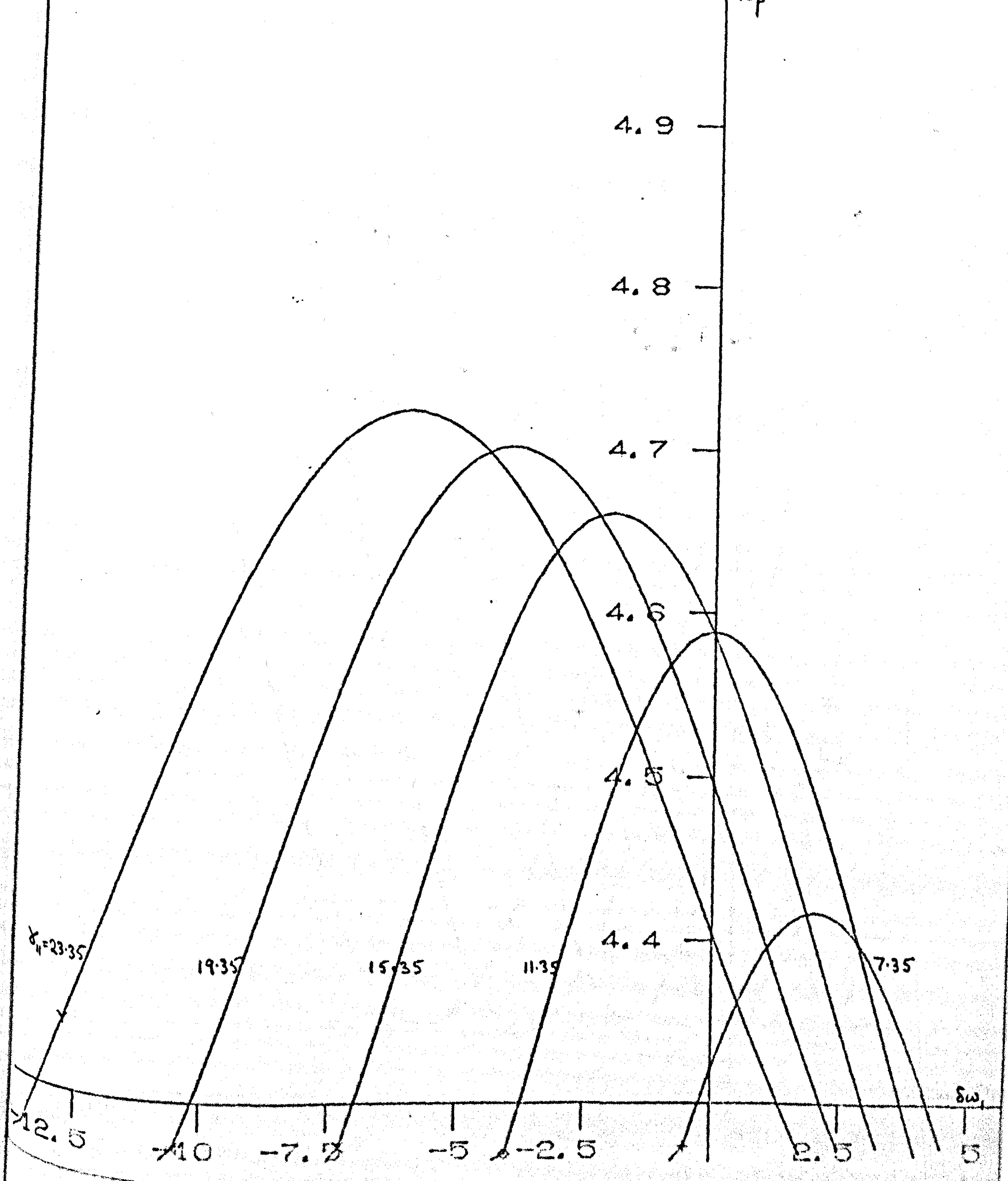


GRAPH No. 13 : E_α v. $\delta\omega_1$

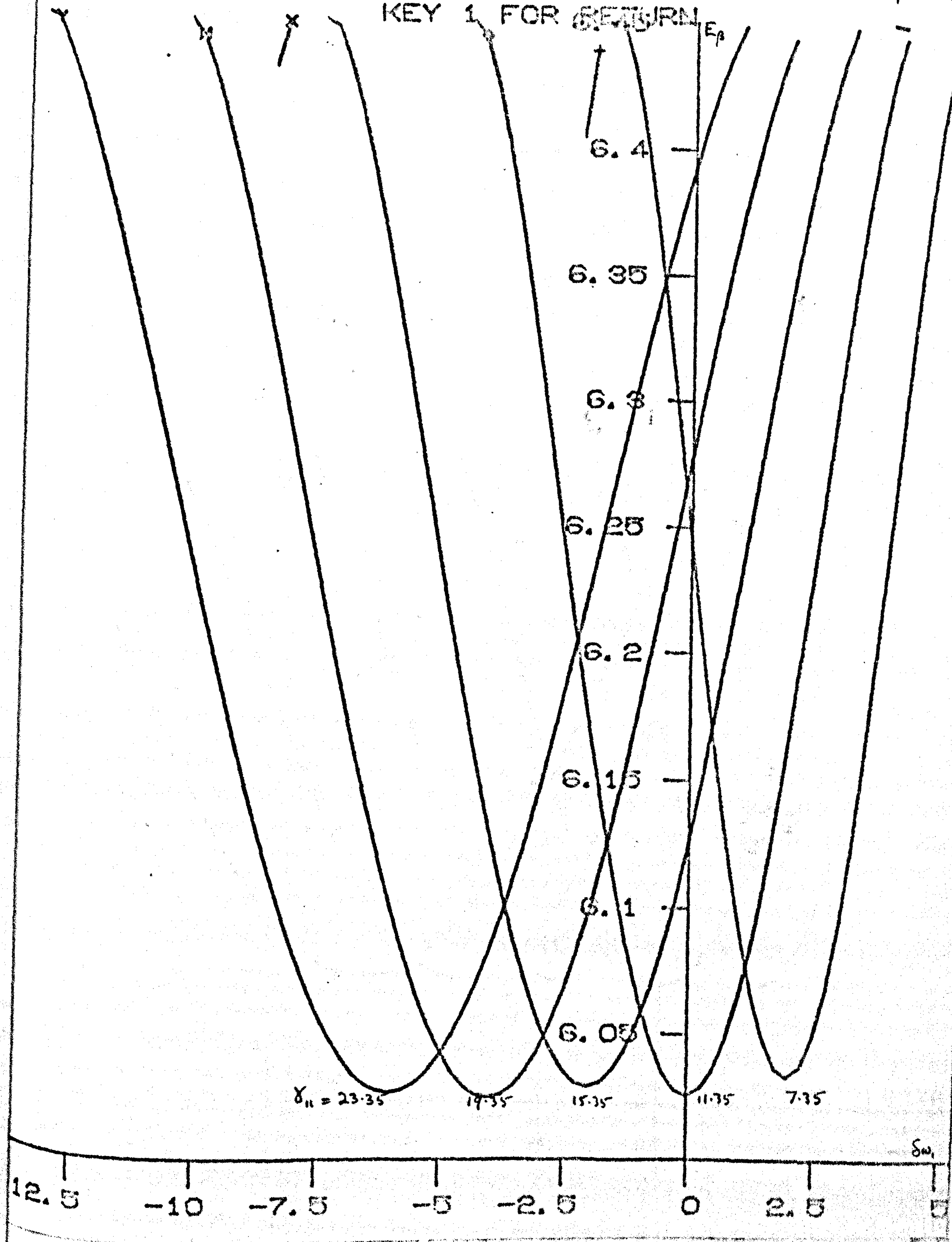


GRAPH No. 14 : E_p v. $\delta\omega_1$

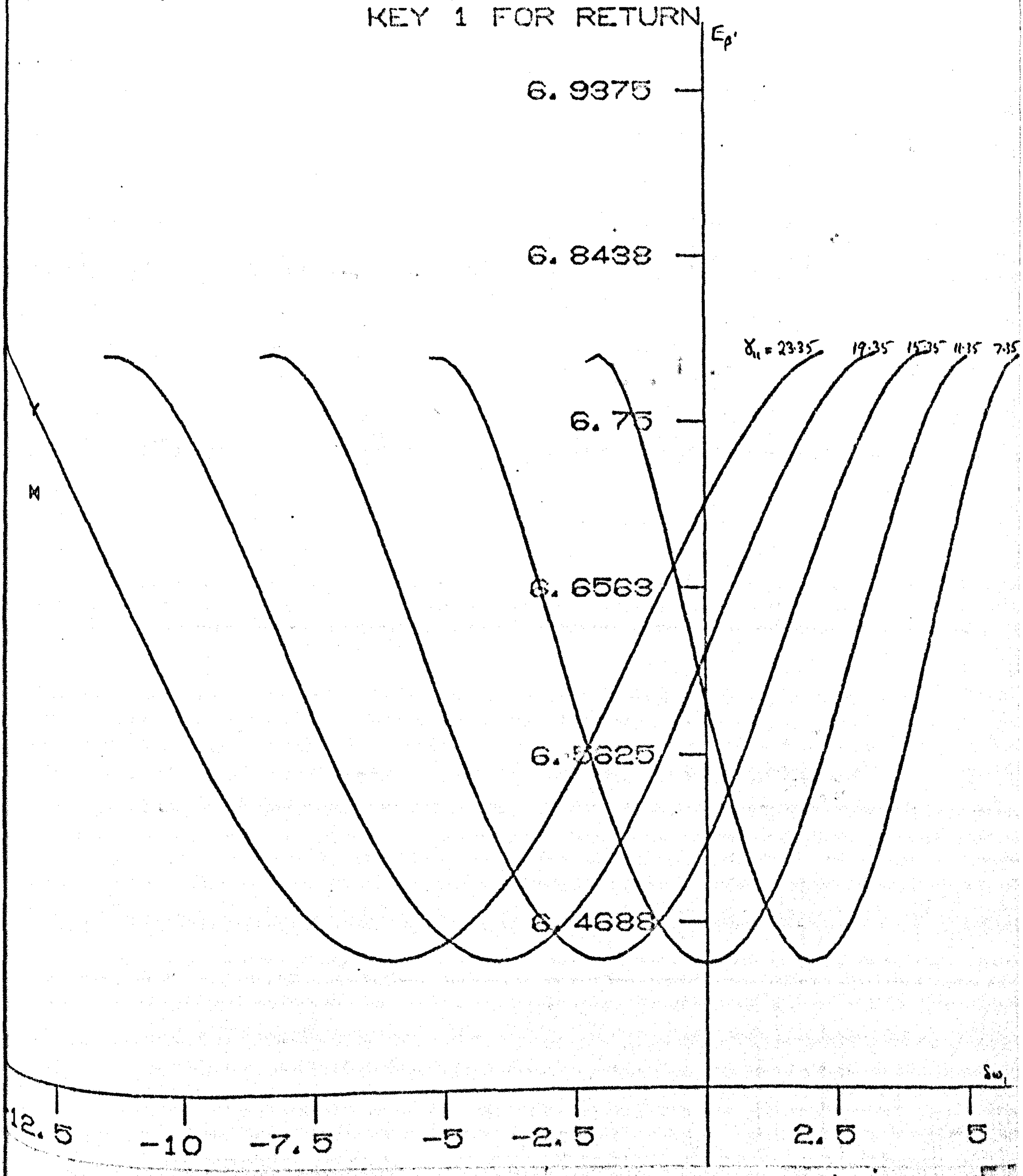
KEY 1 FOR RETURN



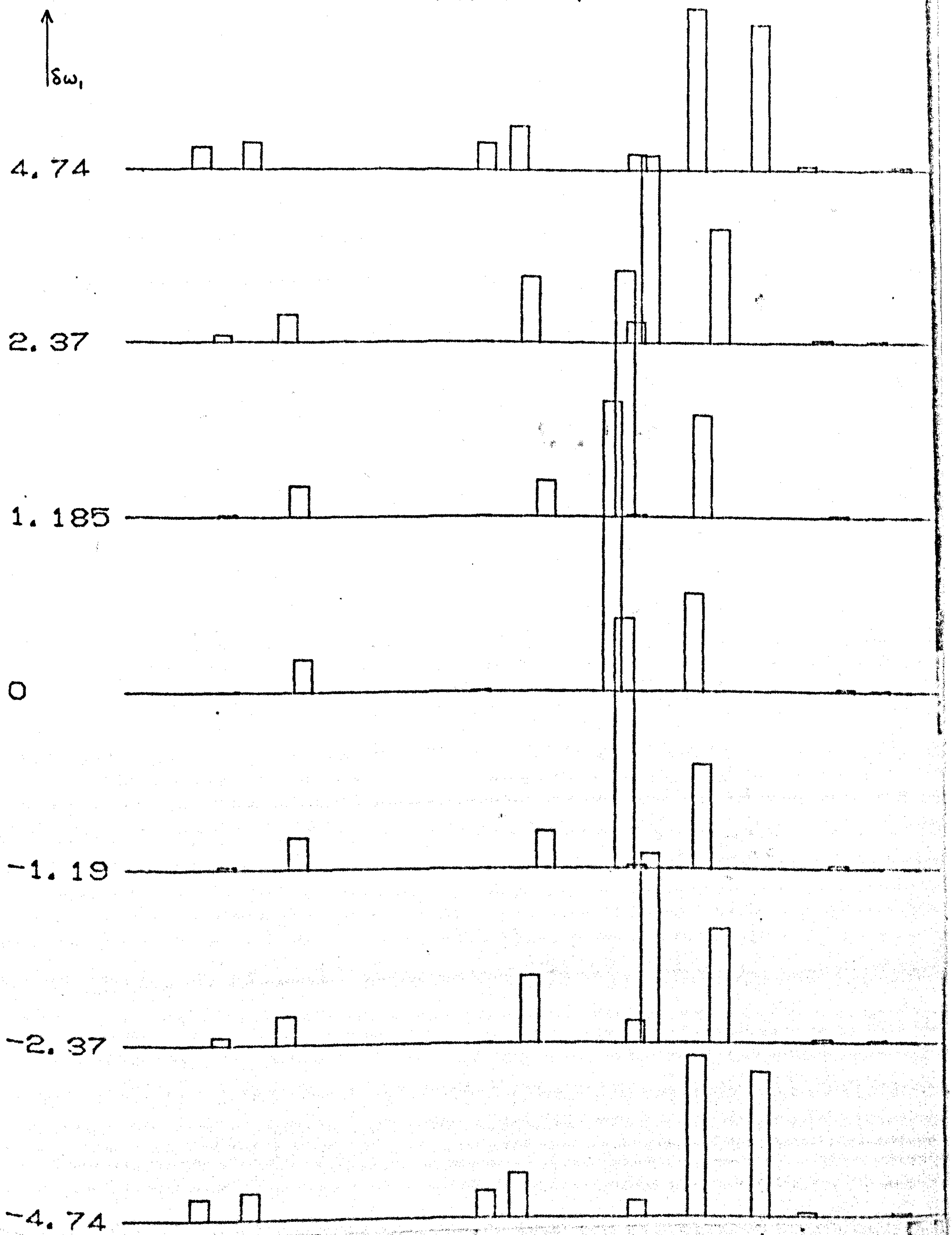
GRAPH No. 15 E_β v. $\delta\omega_1$



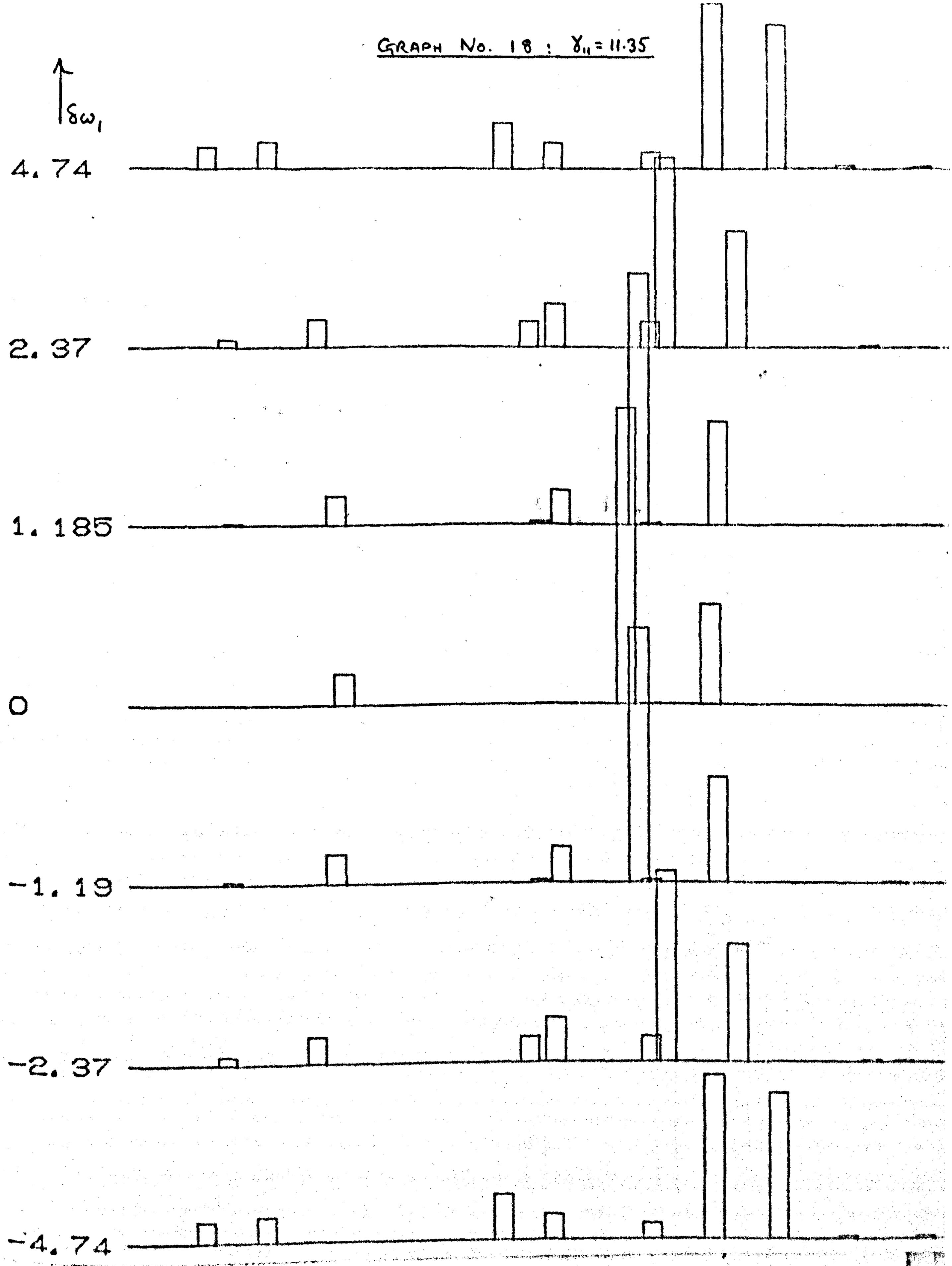
Graph No. 16: $E_{\beta'}$ v. $\delta\omega_1$



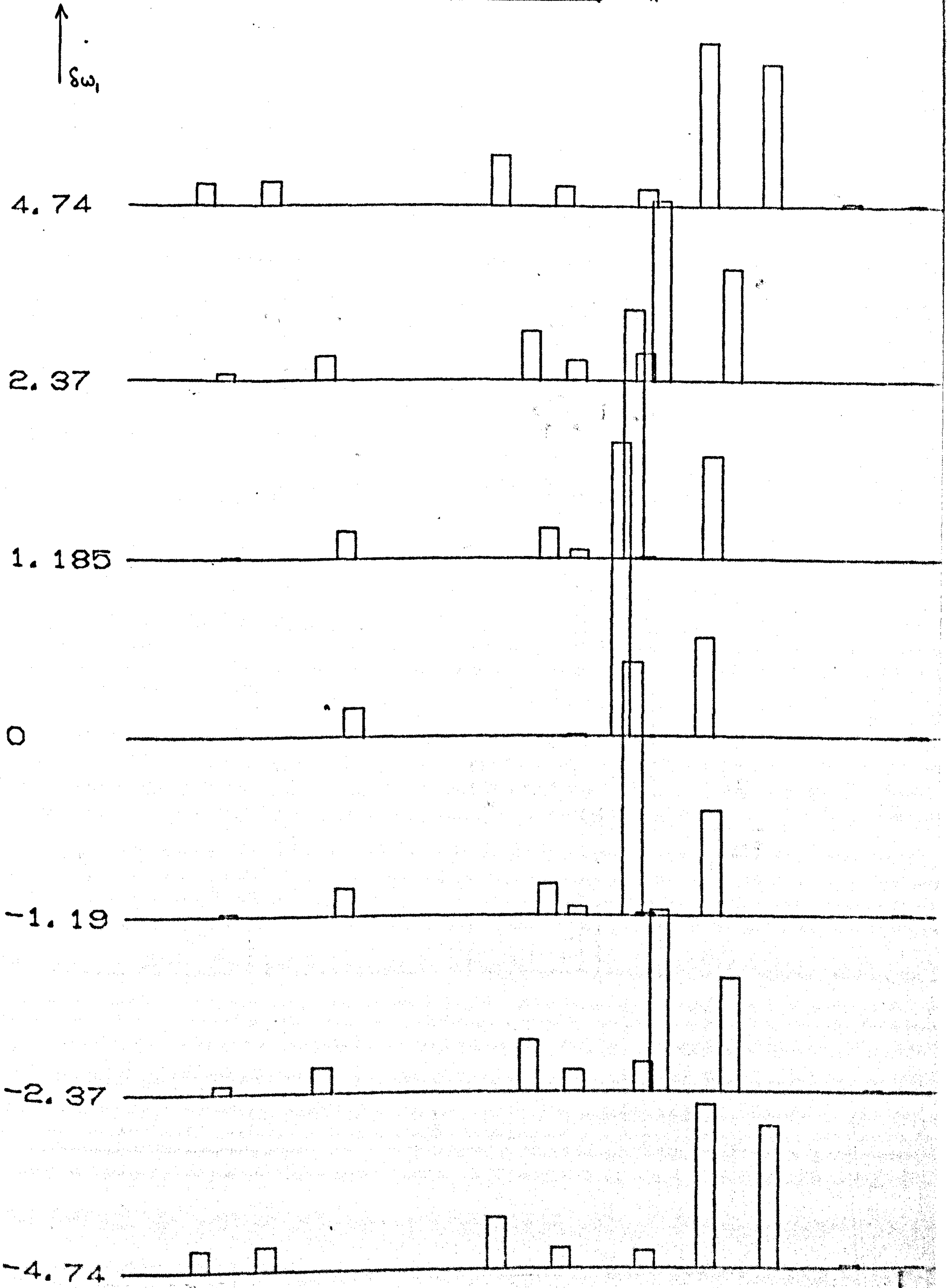
Graph No. 17 : Spectra, $\gamma_{11} = 7.35$

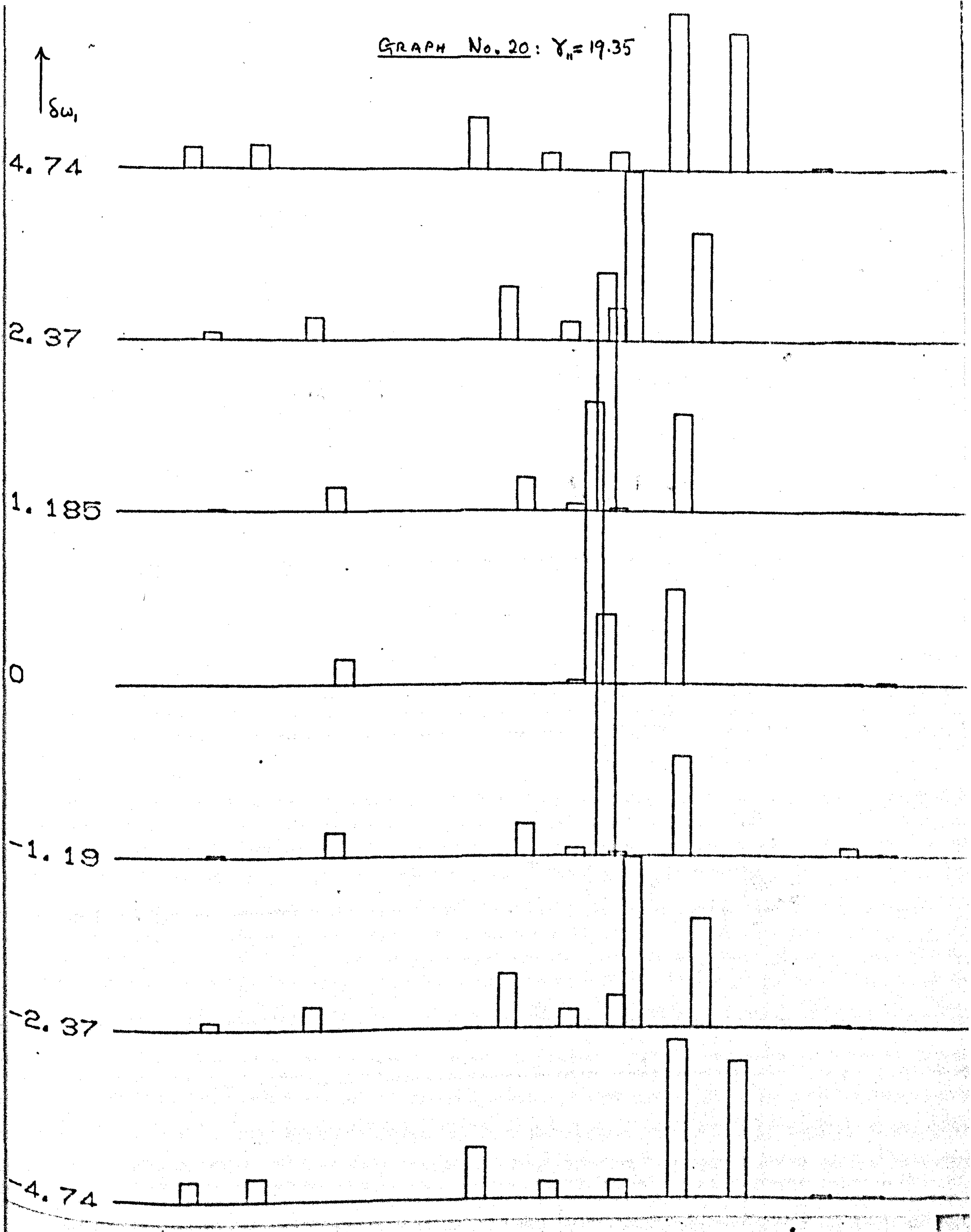


GRAPH No. 18 : $\gamma_{11} = 11.35$



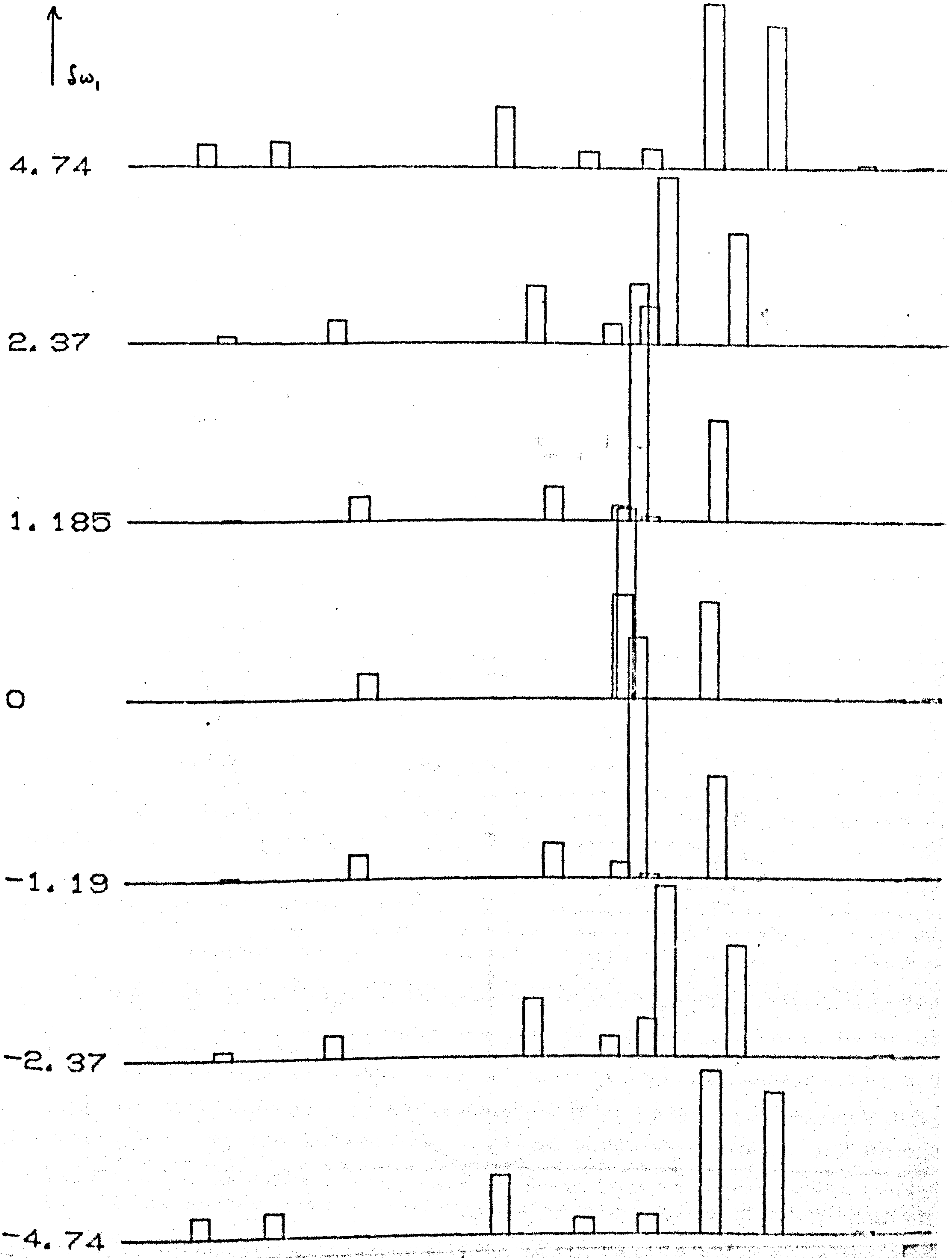
GRAPH No. 19: $\gamma_{11} = 15.35$



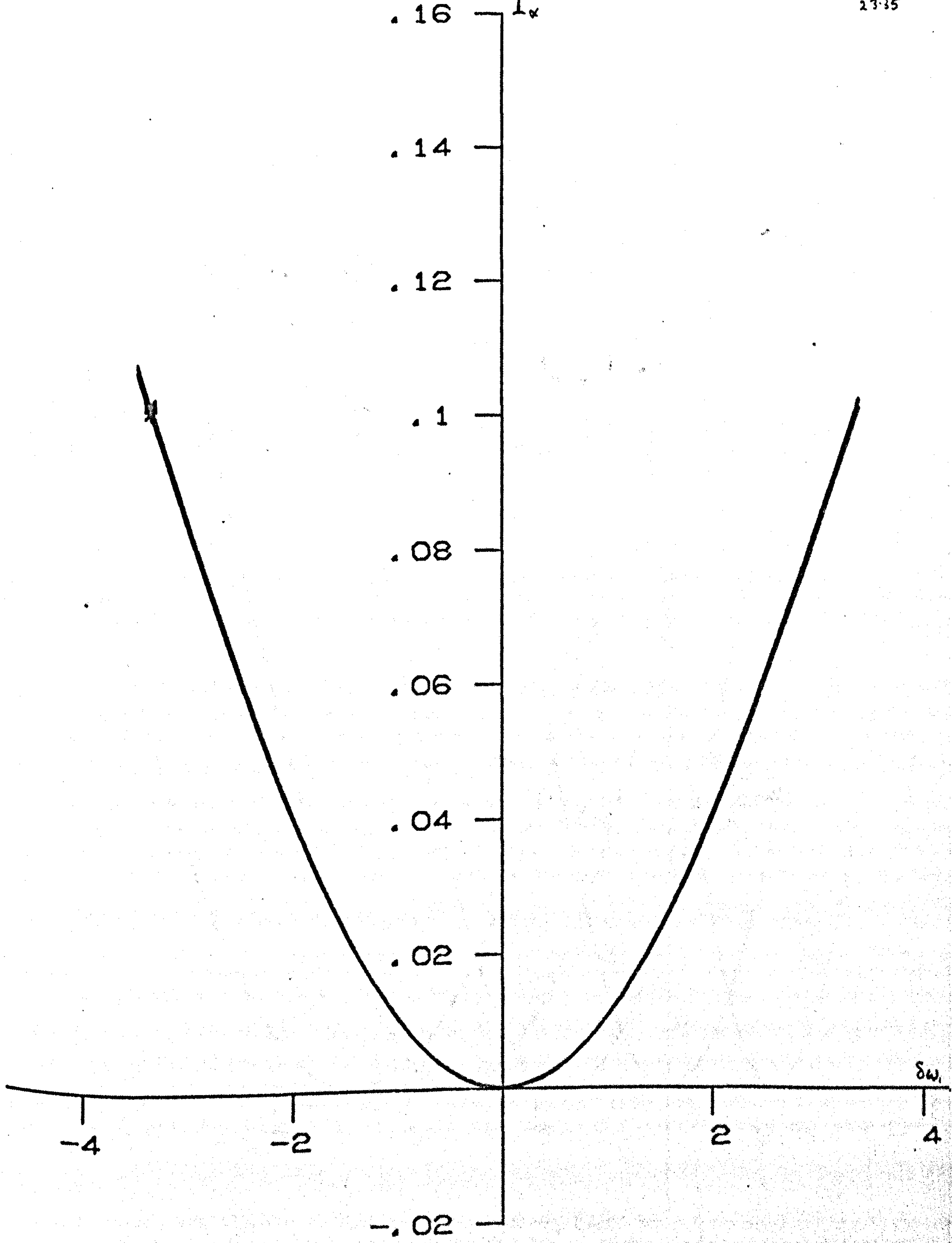


Graph No. 20: $\gamma_{\parallel} = 19.35$

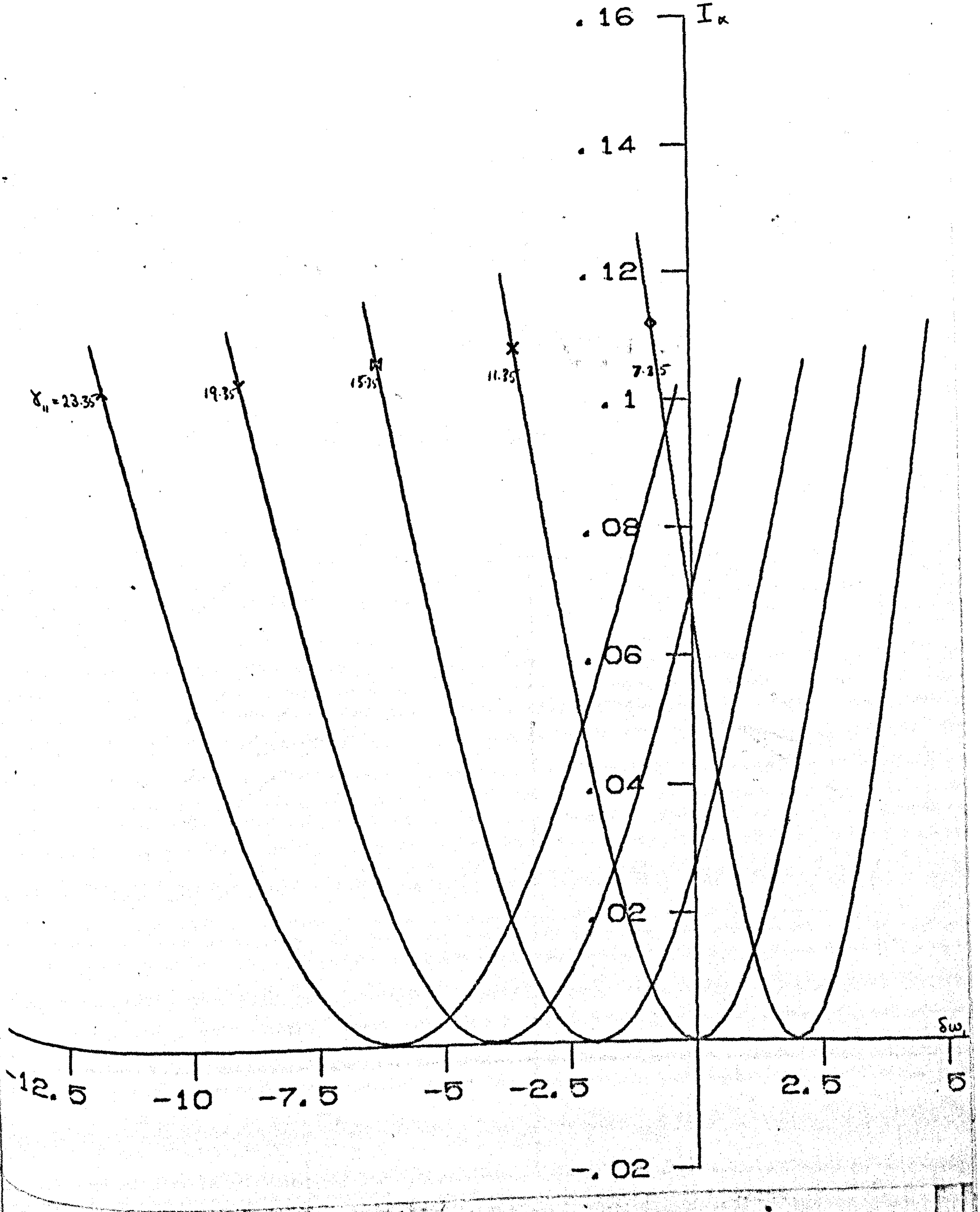
GRAPH No. 21: $\gamma_{11} = 23{\cdot}35$



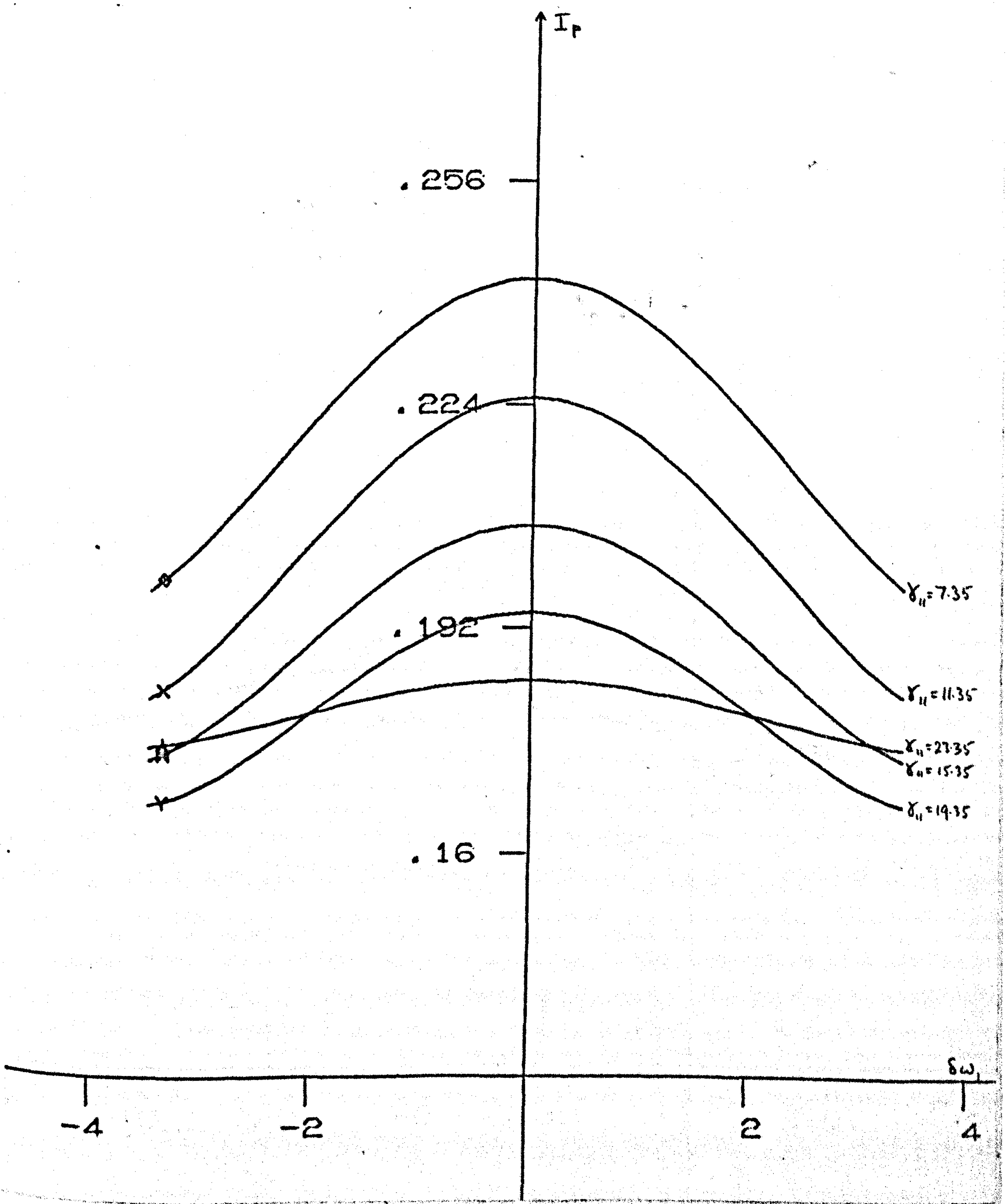
GRAPH No. 22: I_α v. $\delta\omega_1$, $\gamma_{11} = 7.35, 11.35, 15.35, 19.35, 23.35$



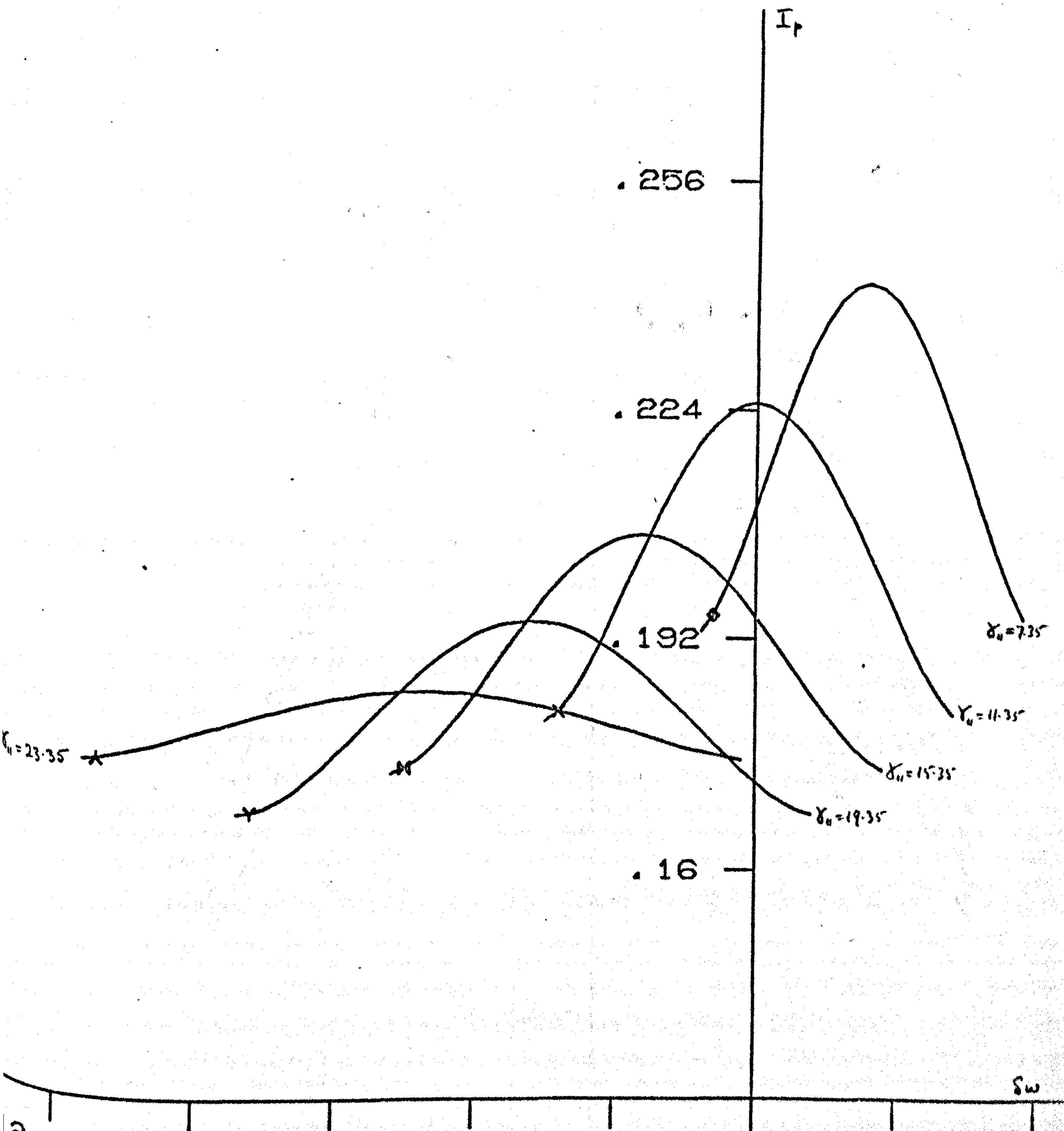
GRAPH No. 23 : I_α v. $\delta\omega_1$



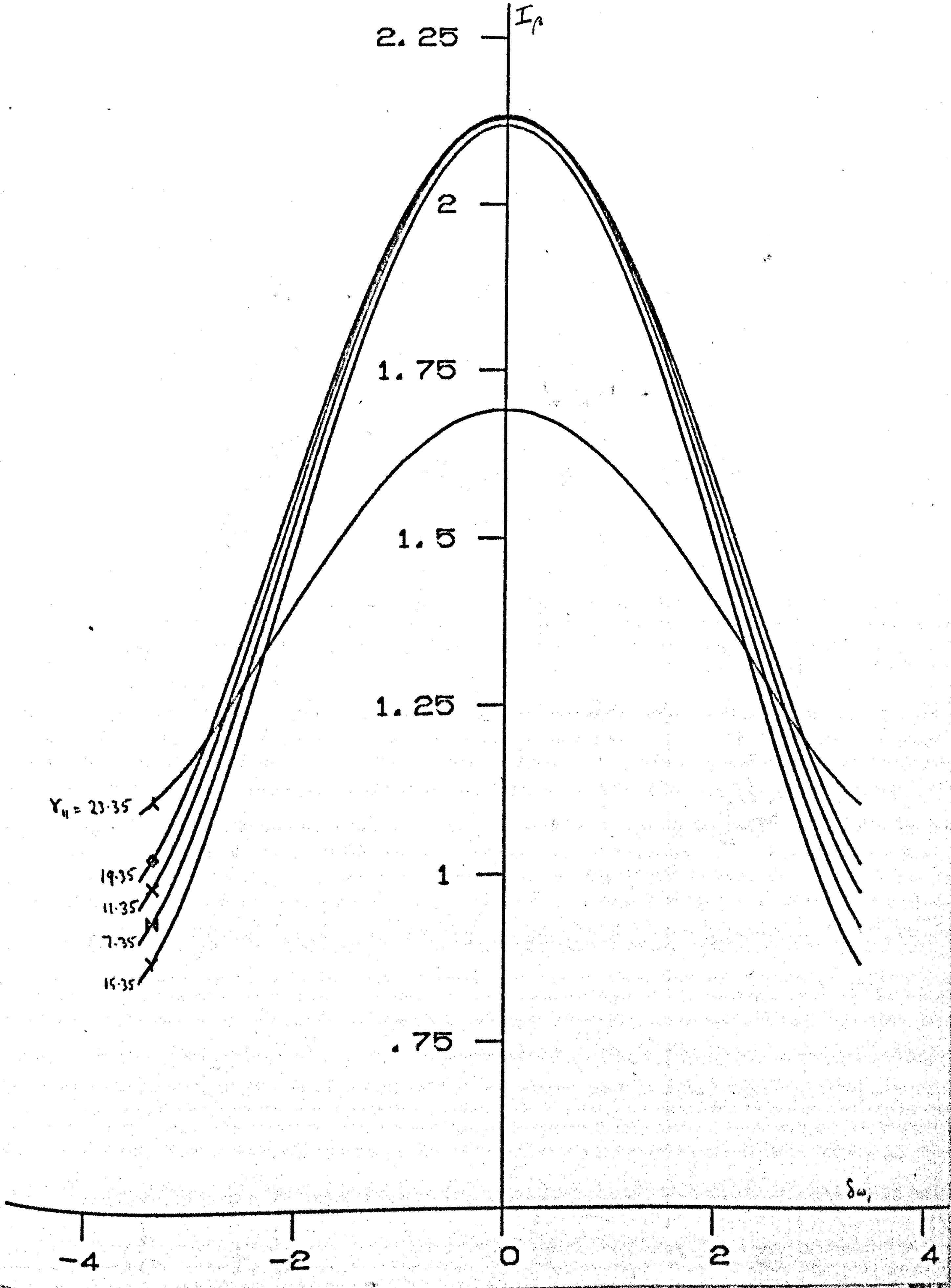
GRAPH No. 24: I_p v $\delta\omega_1$



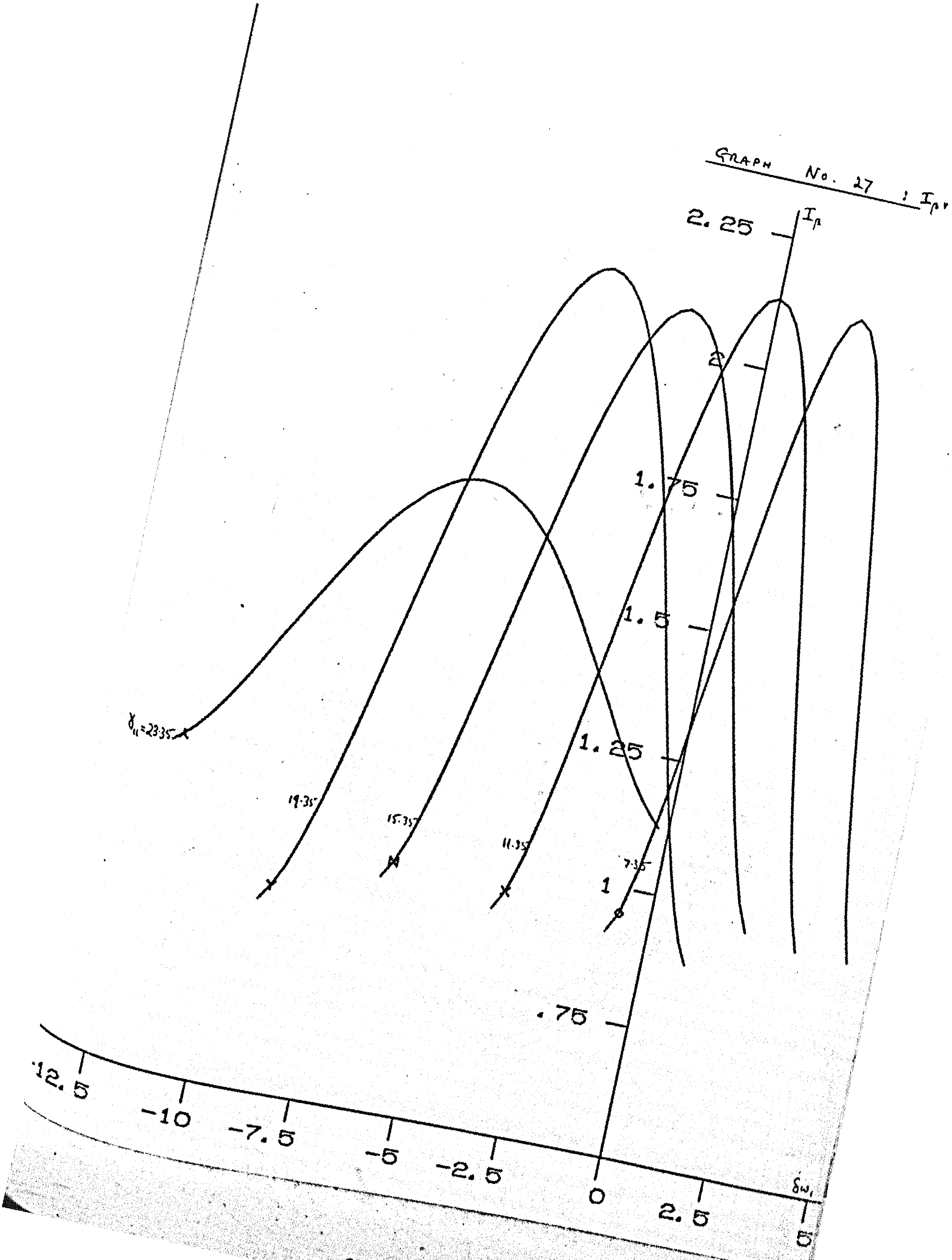
GRAPH No. 25: I_p v. $\delta\omega$



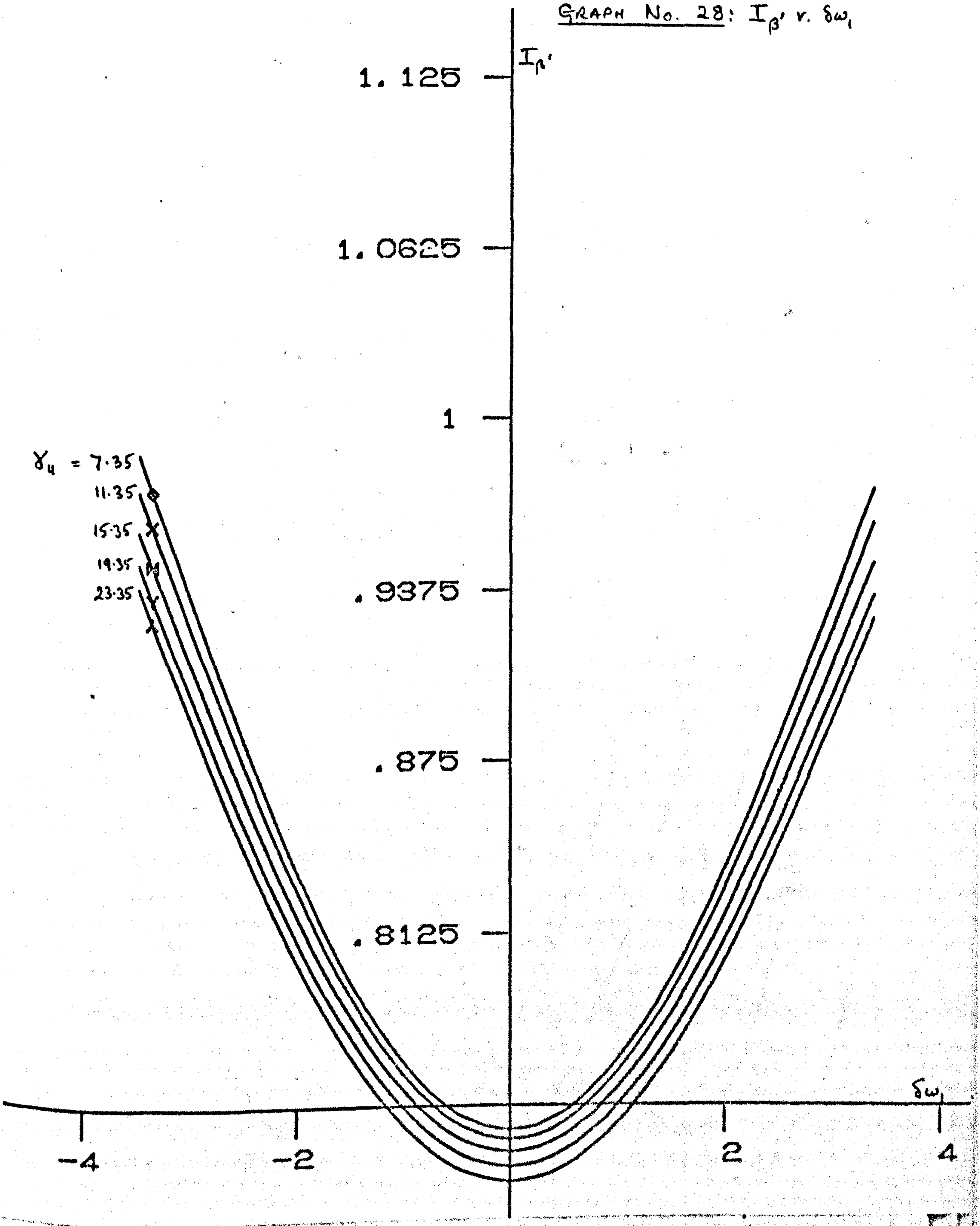
GRAPH No. 26: I_β v. $\delta\omega_1$

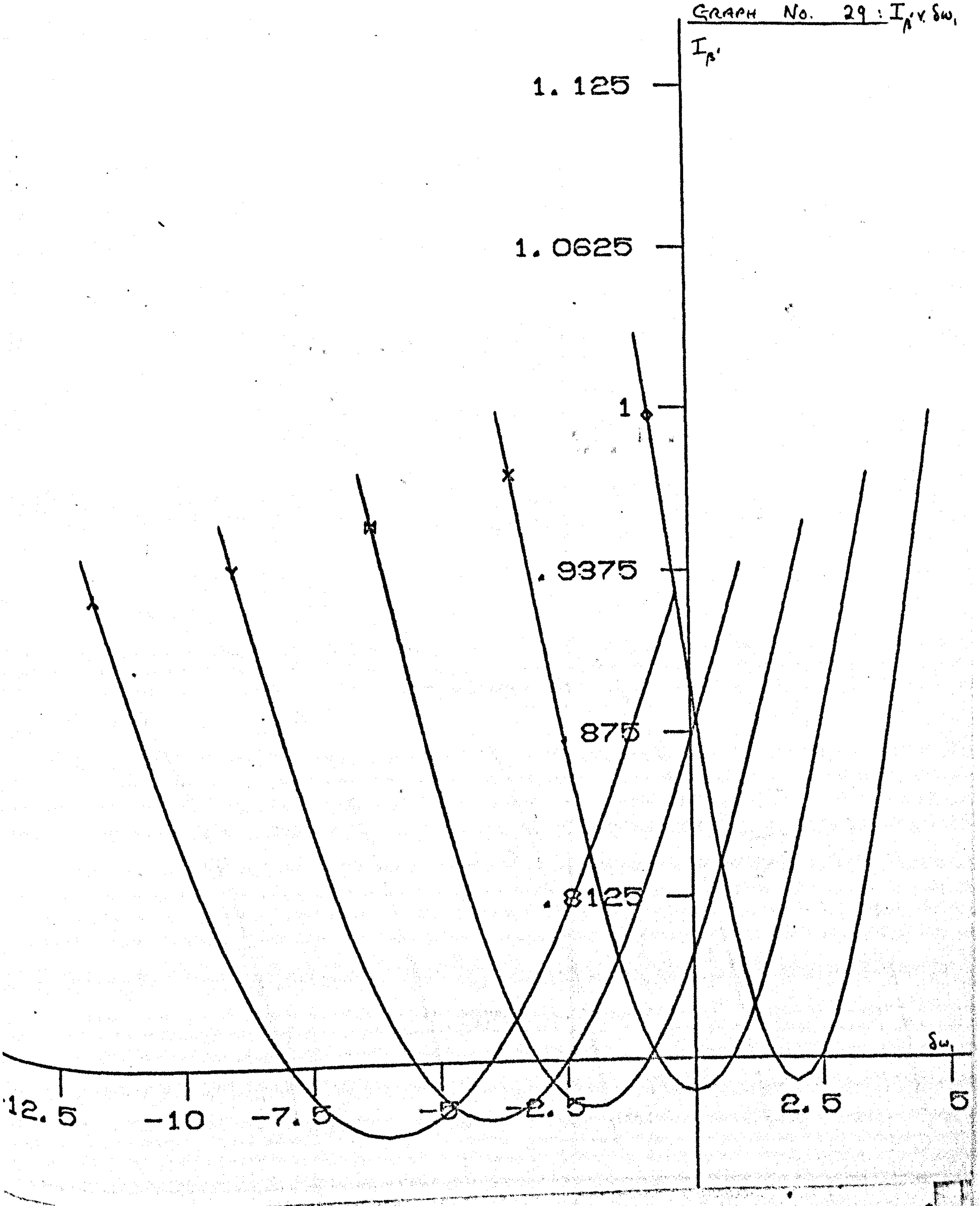


GRAPH No. 27 : I_p v $\delta\omega_1$



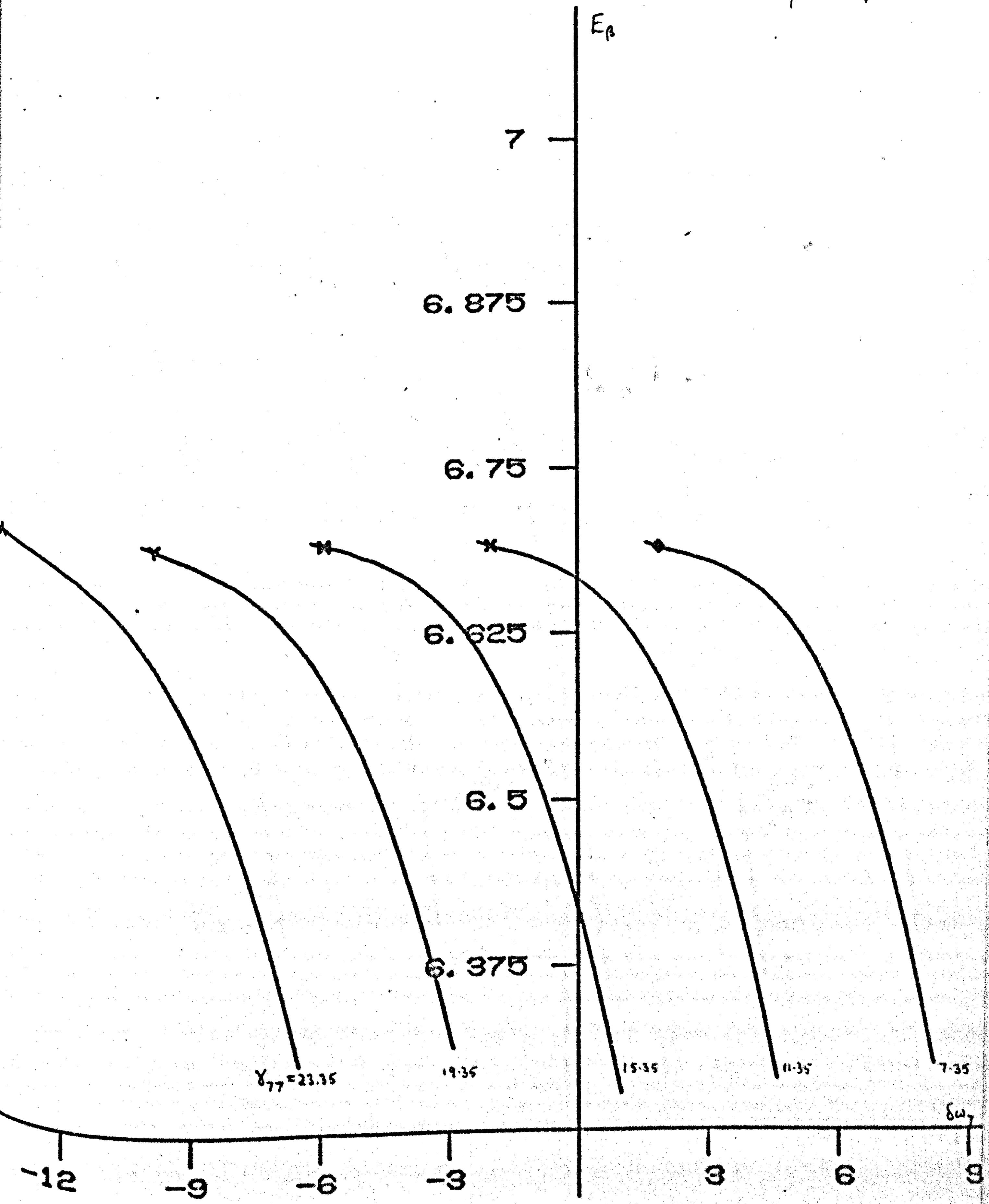
GRAPH No. 28: $I_{\beta'}$ v. $\delta\omega_1$



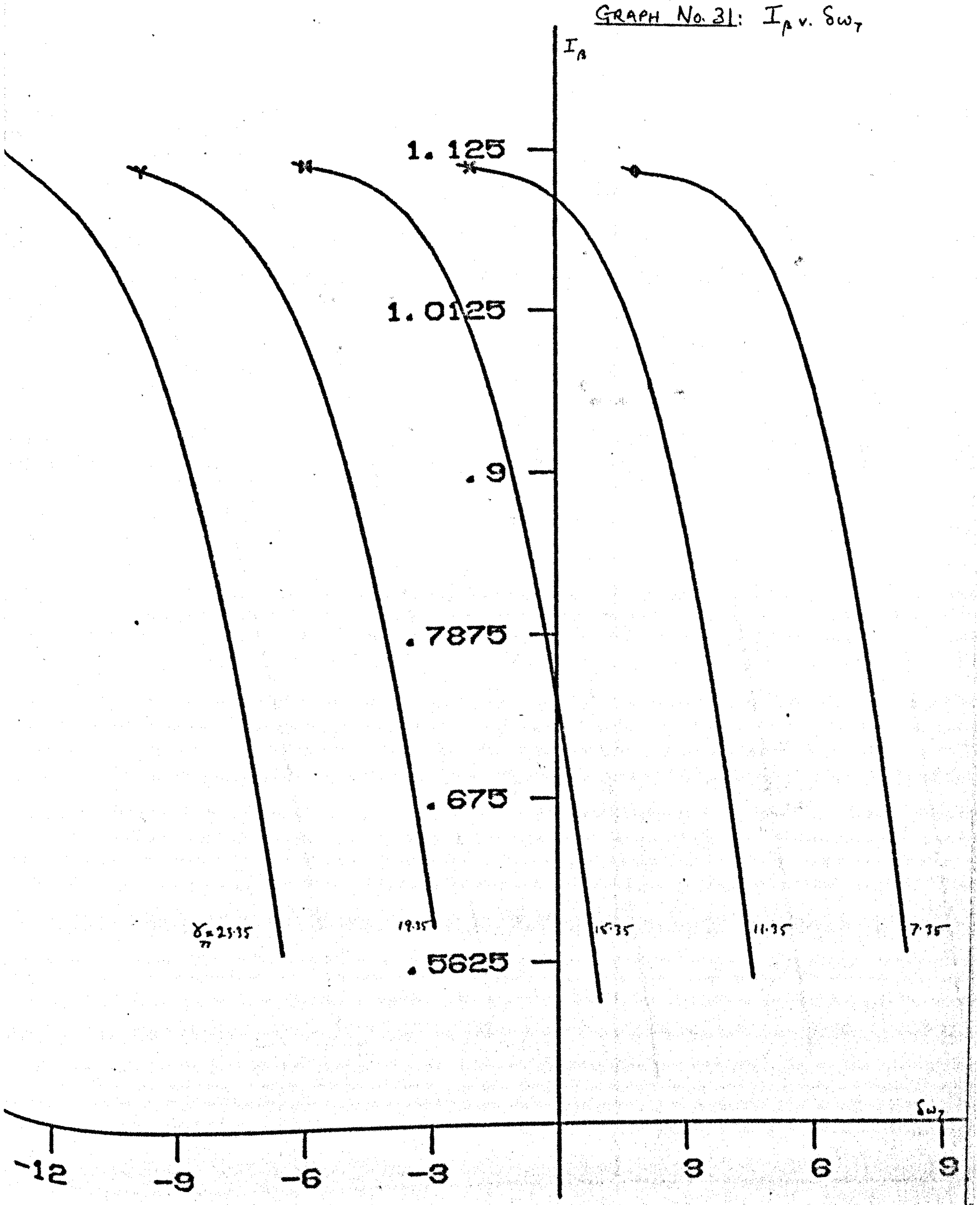

GRAPH No. 29 : $I_{\beta'}$ v. $\delta\omega_1$
$I_{\beta'}$
1.125
1.0625
1
.9375
.875
.8125
$\delta\omega_1$
-12.5
-10
-7.5
-5
-2.5
2.5
5

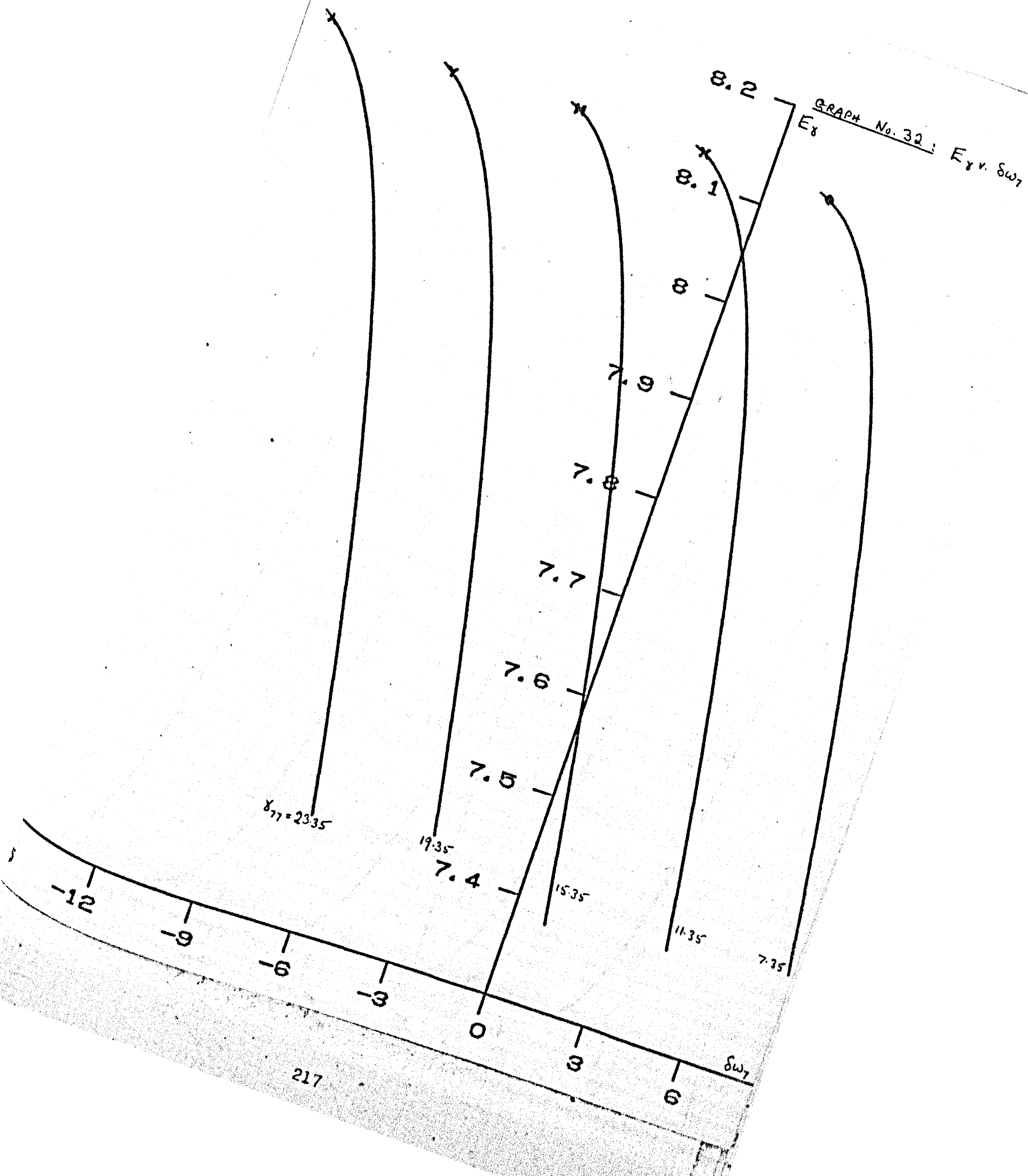
ANILINE

GRAPH No. 30: E_β v. $\delta\omega_7$



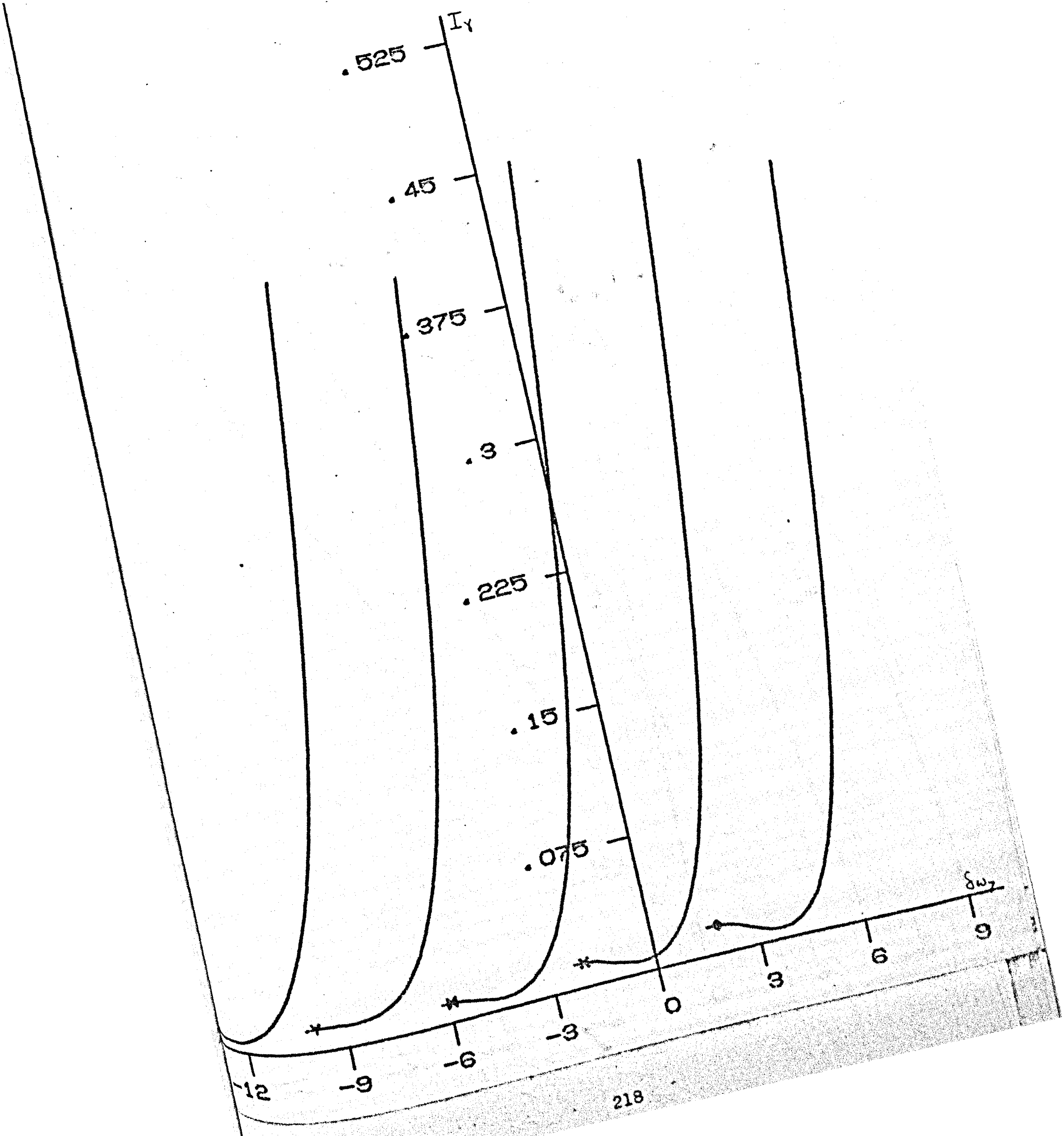
GRAPH No. 31: I_β v. $\delta\omega_T$



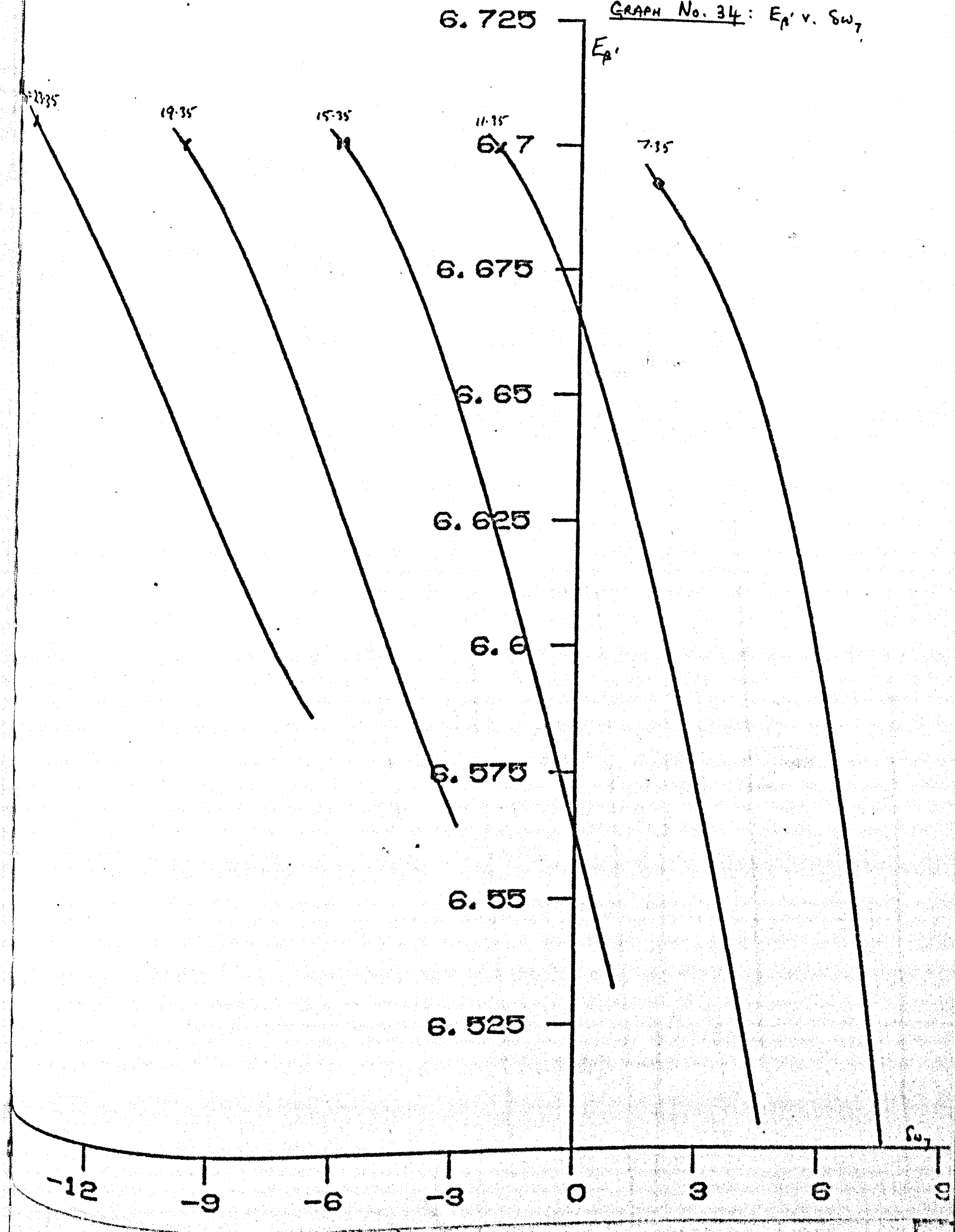


GRAPH No. 32: E_γ v. $\delta\omega_7$

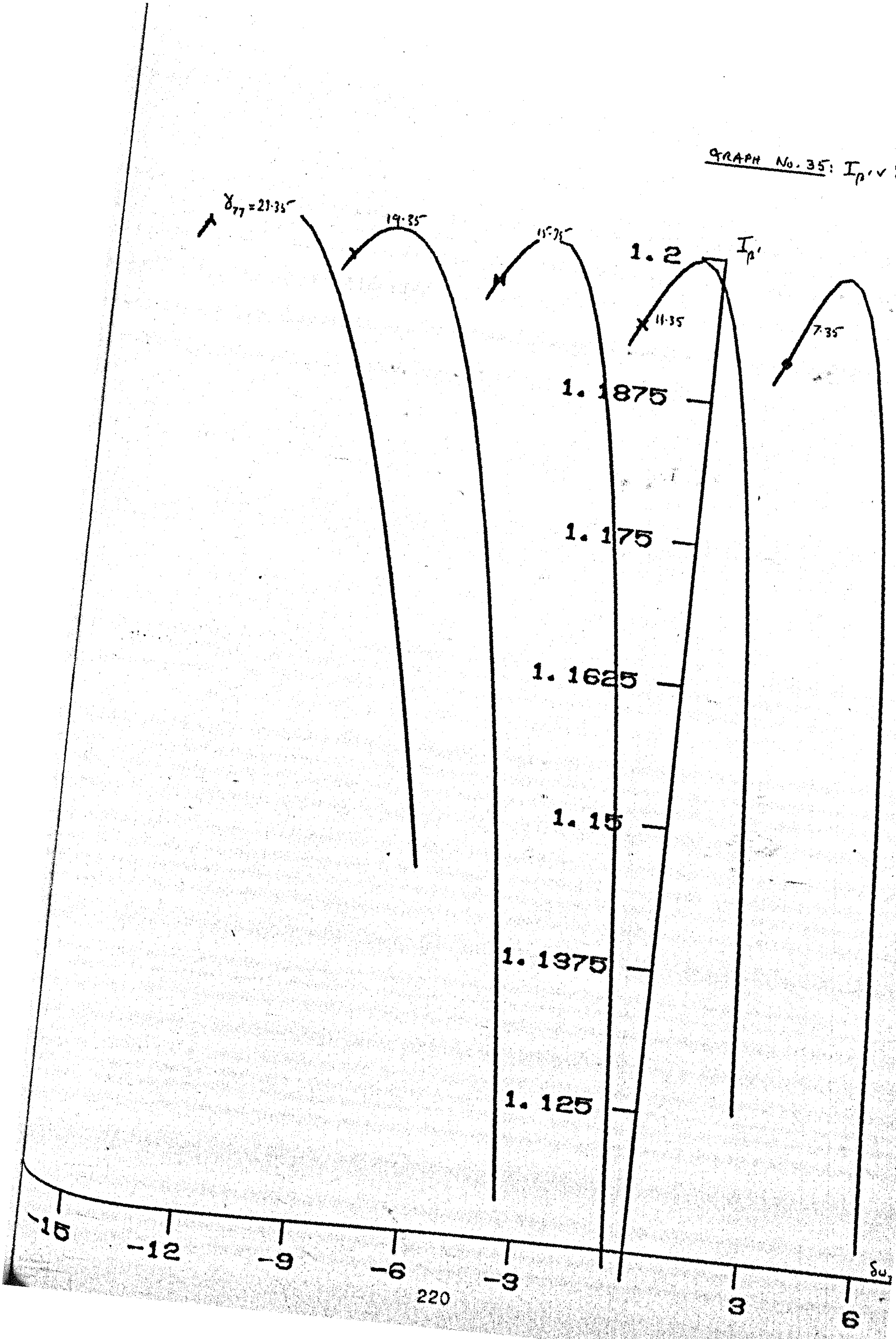
GRAPH No. 33: I_γ v. $\delta\omega_\gamma$



GRAPH No. 34: $E_{\beta'}$ v. $\delta\omega_7$



GRAPH No. 35: $I_{p'}$ v $\delta\omega_7$



5.5 References

{1} Greenwood, H H and Hayward, T H J: Mol. Phys., 3, p495 (1960)

{2} Dierckson, G and McWeeny, R: J. Chem. Phys., 44, p3554 (1966)

{3} Clar, E: "Aromatische Kohlenwasserstoffe", Springer-Verlag, Berlin (1941)

{4} Klevens, H B and Platt, J R: J. Chem. Phys., 17, p470, (1949)

CHAPTER SIX

d_{π} - p_{π} BONDING IN PHOSPHONITRILIC COMPOUNDS - THE HUCKEL APPROXIMATION

An attractive and powerful feature of an interactive graphics system used in scientific research is its potential to accelerate and to extend the scope of the conventional computational approach, as applied to problem solving and to the resolution of questions concerning the interpretation of theoretical models. Solutions arising out of computer calculations can be selected, compared and analysed much more quickly and easily with the aid of graphics. Thus a broader, more thorough experimental background may be established and used as a basis for theoretical deductions. With a flexible, comprehensive graphics system, results obtained and verified analytically can sometimes be incorporated as model refinements, thus extending the computational and analytical capabilities of the system.

This chapter, and the following chapter, contain theoretical studies, at different levels of approximation, of the problem of describing the π-bonding in phosphonitrilic compounds. The origin of the study lies partly in observations and deductions connected with conventional computer calculations, and partly in a consideration of the problems associated with developing the graphics system to investigate and display properties of a class of molecular models less well understood than those of the 'prototype' molecules utilised in earlier chapters.

The current chapter begins with a brief review of the theories and conclusions arrived at by other workers. This is followed by a discussion of the Huckel molecular orbital description of the d_π - p_π cyclic and linear systems, given in relation to a general analytical solution. This solution is derived, using a purely algebraic approach, in a separate section at the end of the chapter. It is accompanied by a general analysis of parameter variations which would not appear to be available within the alternative group theoretical approach, since symmetry is destroyed.

The results obtained in this chapter provide a foundation for computational and analytical investigations into the same problem within the SCF approximation. These will be described in the next chapter, along with the derivation and discussion of analytical properties of certain CI solutions.

6.1 Background to the Problem

In a general review of the structure and reactions of phosphorus chemistry, Paddock, {1}, suggests that interest in phosphonitrilic derivatives has two main sources. The first is the existence of high polymers; the cyclic halides, for instance, form rubber-like solids on heating and it is known that polymers with other attached groups can also be prepared, many of them being untypically resistant to high temperatures and to chemical attack. The second source of interest lies in the distribution of electrons in both the cyclic and the linear molecules and the way this affects molecular configurations, the mechanisms of substitution reactions, and the positions of the groups so introduced.

The present work is concerned exclusively with ideas and developments in this second area of interest, taking the phosphonitrilic halides $(PNX_2)_n$, which exist in both cyclic and linear forms, as examples for study. In both forms conjugation effects can be transmitted through overlap of phosphorus $3d_{xz}$ and $3d_{yz}$, and nitrogen $2p_z$ atomic orbitals of π-type symmetry. Various workers have assumed different basic forms or different degrees of involvement for these atomic orbitals. The alternative assumptions, reflected in the treatment of model parameters in the Huckel molecular orbital approximation, have given rise to apparently divergent solutions and hence to conflicting interpretations of the nature of the $d_\pi - p_\pi$ bonding in these molecules.

The model proposed by Craig and Paddock, {2}, completely ignored $P(3d_{yz})$ orbital participation in conjugation, leading to solutions which suggested π electron delocalisation throughout the PN framework. Dewar, Lucken and Whitehead, {3}, did not consider it justifiable to ignore the d_{yz} orbitals and proposed a model in which they were included with a specific weighting and orientation with respect to the d_{xz} orbitals. Their solutions denied the π electron delocalisation concept of Craig and Paddock, suggesting instead that the π electron distribution was in the form of independent three-centre P-N-P 'island' molecular orbitals, each accommodating two π electrons, with conjugation effects interrupted at each P atom in the molecule.

Although the two rival theories give largely dissimilar predictions, they clearly differ only in the choice and treatment of basic model parameters. Craig and Mitchell, {4}, have shown that, under conditions in which the coulomb parameters of the two phosphorus atomic orbitals are equal, and the two corresponding resonance integrals associated with neighbouring nitrogen atomic orbitals have the same absolute magnitude, the two descriptions are equivalent, differing only by an orthogonal transformation of basis. Recently Doggett, {5}, in an attempt to show that the two approaches do not differ in any fundamental way, has deduced a requirement for obtaining localised islands in terms of certain relationships connecting coefficients of non-localised molecular orbitals. However, these relationships correspond precisely to the conditions previously stated by Craig and Mitchell, which have a more basic significance, since they are related to the definition of the secular equations themselves.

In the following sections of this chapter, properties of the secular equations and of their solutions will be described in terms of a completely general algebraic analysis. The approach taken here differs from the group theoretical approach often adopted, in so much as the limiting constraints on parameters, essential in order to achieve symmetry in the group theoretical methods, need not be applied. This algebraic approach to the problem, supported strongly by computational evidence, permits a more general model to be considered, which essentially embraces all the other, simpler, models constructed within the Huckel approximation. Thus it becomes possible to compare, using one general model, each of the two main theories described above and to analyse the equivalent forms of solutions arising from the degenerate situation which occurs as a result of assumptions made in the simpler models.

The general algebraic solution simplifies, under conditions described by Craig and Mitchell, to a simple formula for the roots, from which the island orbitals can be written down directly. Non-localised symmetry molecular orbitals can then be derived by a simple transformation. These are just two of the infinite number of equivalent forms arising from the degenerate situation, and alternative solutions of theoretical, and possibly of physical interest, are to be described in terms of molecular orbitals associated with groups of islands.

6.2 Solutions of the Secular Equations

Let the $(PN)_n$ cyclic systems be labelled as shown in figure 6.1 where P(3dyz) atomic orbitals are numbered as 1,4,7,..., P(3dxz) as 2,5,8,..., and N(2pz) as 3,6,9,..., with the site axes of the orbitals also as shown.

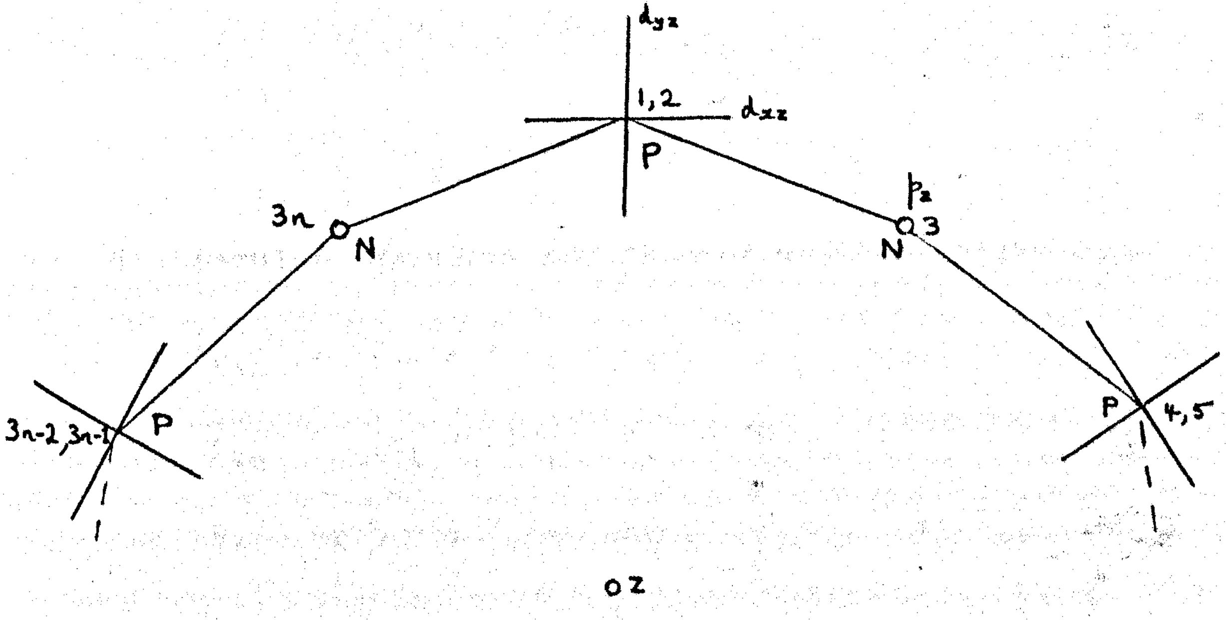


Fig. 6.1.

The general solution derived in section 6.5, is given in terms of coulomb integrals α_{yz}, α_{xz} and α_z for the d_{yz}, d_{xz} and p_z atomic orbitals respectively and in terms of the two resonance integrals

$$\beta_1 = \int \phi(d_{yz}) h_\pi \, \phi\,(p_z) d\tau$$

and

$$\beta_2 = \int \phi(d_{xz}) h_\pi \, \phi\,(p_z) d\tau \qquad -(1)$$

In the rest of this section, as in the work of Craig and Dewar, it will be assumed that $|\beta_1| = |\beta_2|$, since the solutions of theoretical interest which are to be examined arise under this condition. Whereas d_{yz} orbitals match p_z in the region of effective overlap, d_{xz} match on one side of a P atom and mismatch on the other. Resonance integrals β_1 are, therefore, always positive, but β_2 is positive in relation to a p_z orbital on one side of a given P atom, and negative on the other.

Without further loss of generality β_1 may be chosen as the unit of energy and α_z as the zero of energy, so that

$$\alpha_{yz} = \alpha_1 + \alpha_z$$

and

$$\alpha_{xz} = \alpha_2 + \alpha_z \qquad -(2)$$

The secular equations can then be written in the form

$$c_{3n} + (\alpha_1 + x)c_1 + c_3 = 0 \qquad (a)$$

$$c_{3n} + (\alpha_2 + x)c_2 - c_3 = 0 \qquad (b)$$

$$c_1 - c_2 + xc_3 + c_4 + c_5 = 0 \qquad (c)$$

$$- - - - - - - - - - - - - - -$$

$$c_3 + (\alpha_1 + x)c_4 + c_6 = 0 \qquad (d) \qquad -(3)$$

etc.

Solutions to (3) can be expressed in terms of the roots of the cubic

$$p(x) \equiv x^3 + (\alpha_1 + \alpha_2)x^2 - (4 - \alpha_1\alpha_2)x - 2(\alpha_1 + \alpha_2) \qquad -(4)$$

(which is a simplified version of the general cubic derived in section 6.5) and in terms of a parameter

$$\gamma = \alpha_1 - \alpha_2 \qquad -(5)$$

representing the difference in coulomb integrals of the two phosphorus d-orbitals.

When $\gamma = 0$, the secular determinant $P_n(x)$ for the cyclic systems becomes identically equal to $\{p(x)\}^n$, giving n-fold degeneracy in the three roots of $p(x) = 0$.

Writing $\alpha = \alpha_1 = \alpha_2$, the cubic (4) factorises into $(x + d)(x^2 + \alpha x - 4)$ and the required roots are, therefore,

$$-\alpha \quad \text{and} \quad (-\alpha \pm \sqrt{\alpha^2 + 16})/2 \qquad -(6)$$

This special case ($\gamma = 0, |\beta_1| = |\beta_2|$) gives rise to the n-fold degeneracy and defines the condition stated by Craig and Mitchell for equivalence between the island and the delocalised molecular orbital descriptions. In fact, the island model is obtained as a solution of the secular equations only when these conditions on γ and the resonance integrals hold. If, in addition, α is set equal to zero, the island orbitals reduce to the form originally given by Dewar, Lucken and Whitehead.

6.2.1 Derivation of Island Orbitals

Island orbitals can be derived formally by following the algebraic procedures in section 6.5. It is possible, however, to obtain the island orbital expressions in a straightforward manner by imposing the appropriate conditions directly on the secular equations. This procedure also possesses the advantage of illustrating the arbitrariness involved in obtaining one form of solution from the many forms available in a degenerate situation.

Orbitals for the first island of figure 6.1 incorporate the atomic orbitals ϕ_i (i = 1,...,5) with non-zero coefficients only, and take the form

$$\psi = a(\phi_1 - \phi_2) + b\phi_3 + a(\phi_4 + \phi_5) \qquad -(7)$$

Setting $c_{3_n} = 0$ and retaining $\alpha_1 = \alpha_2 = \alpha$, the coefficients c_j and hence a and b in (7) may be found directly from the secular equations (3) as follows -

Equations (3a) and (3b) become

$$(\alpha + x)c_1 + c_3 = 0 \qquad -(8)$$

$$(\alpha + x)c_2 - c_3 = 0 \qquad -(9)$$

which, consistently with (7), give

$$c_2 = -c_1 \qquad -(10)$$

Further progress is made by considering separately the roots $(-\alpha \pm \sqrt{\alpha^2 + 16})/2$ and $-\alpha$.

6.2.1(a) $x = (-\alpha \pm \sqrt{\alpha^2 + 16})/2$

From equation (8)

$$c_3 = -(\alpha + x)c_1 \qquad -(11)$$

and in (3c), two further conditions are necessary for consistency with (7), namely,

$$c_4 = c_5 \qquad -(12)$$

and $$c_4 = c_1 \qquad -(13)$$

It now follows from (3c) that

$$c_3 = -4c_1/x \qquad -(14)$$

which, when substituted in (11) confirms the quadratic form for the two roots. These coefficients, therefore, satisfy the first group of three equations, and substitution in the rest of the equations shows that each is satisfied identically, with the remaining coefficients equal to zero. The normalisation condition now leads to

$$\psi = \frac{x}{2\sqrt{x^2+4}}(\phi_1-\phi_2) \pm \frac{2}{\sqrt{x^2+4}}\phi_3 + \frac{x}{2\sqrt{x^2+4}}(\phi_4+\phi_5) \qquad -(15)$$

as the general form of an island orbital for a root given by

$$x = (-\alpha \pm \sqrt{\alpha^2 + 16})/2$$

where

$$\alpha = \alpha_1 = \alpha_2$$

6.2.1(b) $x = -\alpha$

For this root, equations (8) and (9) give $c_3 = 0$. An island orbital of the form (7) may then be obtained from (3c) provided

$$c_4 = c_5 = -c_1 = c_2 \qquad -(16)$$

Once again the rest of the equations are satisfied identically with the remaining coefficients equal to zero. For the root $x = -\alpha$, the island orbital then has the normalised form

$$\psi = \tfrac{1}{4}(\phi_1-\phi_2) - \tfrac{1}{4}(\phi_4+\phi_5) \qquad -(17)$$

which can be seen to be independent of α.

The conditions (10), (12), (13) and (16) are chosen arbitrarily, apart from conforming with the island orbital form (7) and satisfying the secular equations (3). Other choices can be made leading to other forms of solution, very much different from the island orbitals derived above. The arbitrariness present when making a choice which leads to a valid solution is essentially a consequence of the n-fold degeneracy. It is sufficient when choosing the conditions to ensure that the complete set of coefficients c_j ($j = 1,2,\ldots,3n$) satisfies the secular equations for a given root. The procedure outlined above may be repeated, starting from equation (1d), to give a second similar island, and so on, giving n such islands in all, with the complete set of islands satisfying the secular equations.

6.2.2 Derivation of Island Group Orbitals

A different form of solution from the islands derived in 6.2.1 will now be obtained, by following a similar procedure but by adopting different conditions leading to the relationships between the coefficients.

Proceeding as in 6.2.1(a) but replacing conditions (12) and (13) by

$$c_4 \neq 0, \quad c_5 = 0 \qquad -(18)$$

it is now possible to satisfy the first six equations of (3) by imposing the conditions

$$c_7 = c_8, \quad c_7 = c_1 \qquad -(19)$$

which are analagous to (12) and (13). Once more the complete set of secular equations is satisfied.

An alternative choice to (18), namely

$$c_4 = 0, \quad c_5 = 0 \qquad -(20)$$

is possible and the secular equations can then be satisfied by imposing the conditions

$$c_7 = c_8, \quad c_7 = -c_1 \qquad -(21)$$

The molecular orbitals resulting from the imposition of these two sets of conditions are the same as those obtained by taking linear combinations in sum and difference form of island orbitals belonging to the same eigenvalue, for the first two islands. Thus

$$\psi^{+}_{1,2} = \frac{1}{\sqrt{2}} \left\{ a(\phi_1 - \phi_2) + b\phi_3 + a(\phi_4 + \phi_5) \right\}$$

$$+ \frac{1}{\sqrt{2}} \left\{ a(\phi_4 - \phi_5) + b\phi_6 + a(\phi_7 + \phi_8) \right\}$$

$$= \frac{1}{\sqrt{2}} \left\{ a(\phi_1 - \phi_2) + b\phi_3 + 2a\phi_4 + b\phi_6 + a(\phi_7 + \phi_8) \right\} \quad \text{-(22)}$$

and

$$\psi^{-}_{1,2} = \frac{1}{\sqrt{2}} \left\{ a(\phi_1 - \phi_2) + b\phi_3 + 2a\phi_5 - b\phi_6 - a(\phi_7 + \phi_8) \right\} \quad \text{-(23)}$$

where conjugation effects are transmitted through the $\phi_4(d_{yz})$ orbital in $\psi^{+}_{1,2}$ and through the $\phi_5(d_{xz})$ orbital in $\psi^{-}_{1,2}$. It is therefore possible to obtain molecular orbitals describing a group of two islands, involving ϕ_i ($i = 1,2,..8$) only. In all, six localised group orbitals $\psi_{1,2}$ can be obtained by taking such sum and difference combinations of corresponding island orbitals of the first and second islands. The remaining molecular orbitals may be obtained, as before, as single island orbitals or as analagous group orbitals for island pairs.

Clearly, the process of obtaining combinations can be extended to groups of three, four, or any number of islands. A general solution of the secular equations (3) under the conditions $\alpha_1 = \alpha_2$, $|\beta_1| = |\beta_2|$, for which the island solution holds, can, therefore, be expressed in terms of molecular orbitals that are localised over groups r, s, t,... of islands, where r, s, t etc., can take any non-negative integral value subject only to

$$r + s + t + \ldots = n \quad \text{-(24)}$$

The localised solution for P-N-P islands is, therefore, a special case corresponding to $r = s = t = \ldots = 1$, and a completely delocalised solution implies $r = n$, with $s = t = \ldots = 0$. Whereas the total number of localised forms is restricted by (24), delocalised forms exist in an infinity of solutions.

6.2.3 Derivation of Symmetry Molecular Orbitals

In section 6.2.1 expressions (15) and (17) gave the island orbitals with coefficients in terms of the corresponding roots of the quadratic form (6) which may be evaluated for a given coulomb parameter α. From these a transformation may be made to the corresponding symmetry molecular orbitals.

First collect the island orbitals $\psi_i^{(x)}$ for the n islands $(i = 1,2,\ldots,n)$ corresponding to a common root x $(=x_1, x_2$ or $x_3)$ as the rows of a $3\times n$ matrix $\psi^{(n)}$ given by

$$\psi^{(n)} = \begin{bmatrix} \psi_1^{(x_1)} & \psi_2^{(x_1)} & \ldots & \psi_n^{(x_1)} \\ \psi_1^{(x_2)} & \psi_2^{(x_2)} & \ldots & \psi_n^{(x_2)} \\ \psi_1^{(x_3)} & \psi_2^{(x_3)} & \ldots & \psi_n^{(x_3)} \end{bmatrix} \qquad -(25)$$

Next apply the transformation

$$\phi^{(n)} = \psi^{(n)} U^{(n)} \qquad -(26)$$

where $U^{(n)}$ is a matrix of order nxn with elements

$$U_{rj}^{(n)} = \frac{1}{\sqrt{n}} \exp \frac{2\pi ir(j-1)}{n} \qquad (r,j = 1,2\ldots n) \qquad -(27)$$

$\phi^{(n)}$ is then a $3\times n$ matrix whose rows are the symmetry orbitals corresponding to a common root x, expressed in complex form.

To obtain real coefficients, the elements $U_{rj}^{(n)}$ must take the form (r = 1,2...,n throughout)

$$U_r^{(n)} = \frac{1}{\sqrt{n}}$$

$$U_{rj}^{(n)} = \sqrt{\frac{2}{n}} \cos \frac{2\pi r(j-1)}{n} \quad -(28), \quad j = 2,3..\tfrac{n+1}{2} \text{ (n odd)}$$

$$j = 2,3,.\tfrac{n}{2} \quad \text{(n even)}$$

$$U_{r,n-j+2}^{(n)} = \sqrt{\frac{2}{n}} \sin \frac{2\pi r(j-1)}{n} \quad -(29), \quad j = 2,3..\tfrac{n+1}{2} \text{ (n odd)}$$

$$j = 2,3..\tfrac{n}{2} \quad \text{(n even)}$$

and $U_{r,\frac{n}{2}+1} = (-1)^r \frac{1}{\sqrt{n}}$ -(30), n even.

For the trimer $(PN)_3$, the familiar form

$$U^{(3)} = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{-1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & \frac{-1}{\sqrt{6}} & \frac{-1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \end{bmatrix} \quad -(31)$$

is obtained.

The symmetry orbitals in ϕ can now be written down immediately from the matrix expression (26).

6.3 The Significance of Island Orbitals

Symmetry molecular orbitals and island orbitals are particular forms of solution of the n-fold degenerate problem which can be related to the geometrical structure of the $(PN)_n$ ring.

In practical terms, delocalised orbitals are usually associated with the description of spectroscopic properties, and localised orbitals with the bonding in molecules. In the case of the localised island orbitals of the $(PN)_n$ ring systems, a specific theoretical interpretation can be given in terms of the change in the form of solution when single coulomb integrals are varied. The relevant unperturbed solution is the n-fold degenerate case described by any arbitrary set of eigenvectors, although the general case will be analysed in section 6.5.3.

6.3.1 Variation of a Single Nitrogen Coulomb Integral

Suppose that a single nitrogen coulomb integral is modified from the standard value $\alpha_z = 0$ to a value α_3, say. As a result, the characteristic polynomial P_n changes to

$$P_n' = P_n + d' D_{n-1} \qquad -(32)$$

where P_n and D_n are as defined in section 6.5, and where

$$d' = \alpha_3(x+\alpha_1)(x+\alpha_2) \qquad -(33)$$

Under the condition $\alpha_1 = \alpha_2 = \alpha$, which obtains in the present case, P_n reduces to p^n and $D_{n-1} \equiv P_{n-1} = p^{n-1}$ (since $\gamma = 0$). Hence

$$P_n' = (p+d)\, p^{n-1} \qquad -(34)$$

with

$$p(x) = (x+d)(x^2+\alpha x-4) \qquad -(35)$$

and

$$d(x) = \alpha_3(x+\alpha)^2 \qquad -(36)$$

which means that the original, unperturbed n-fold degeneracy in three roots is modified to give the same three roots in (n-1)-fold degeneracy, with three additional roots given by

$$p(x) + d(x) = 0 \qquad -(37)$$

which may be expanded under the above conditions to give

$$(x+\alpha)(x^2+(\alpha+\alpha_3)x+\alpha\alpha_3-4) = 0 \qquad -(38)$$

with roots

$$x = -\alpha \text{ and } x = \tfrac{1}{2}\left(-(\alpha+2\alpha_3)\pm\sqrt{((\alpha-\alpha_3)^2+16)}\right) \qquad -(39)$$

The (n-1)-fold degeneracy may be described as before by island orbitals in groups, subject to (24) with n replaced by (n-1), or by delocalised molecular orbitals. The three remaining levels which separate out of the degenerate system are described uniquely by localised island orbitals associated with the modified N atom and retaining the forms (15) and (17). The localised orbital (17) corresponds to the root $x = -\alpha$, and remains unchanged under the perturbation. The weights of (15) may be determined by substitution of the roots given in (39).

Thus single island orbitals are zeroth-order orbitals of the n-fold degenerate solution corresponding to a change in coulomb integral of a nitrogen atom.

6.3.2 Variation of a Single P(dyz) or a Single P(dxz) Coulomb Integral

6.3.2(a) P(dyz)

Suppose first that a single phosphorus d_{yz} coulomb integral is modified from the common value α, taken by all the other d-orbital coulomb integrals in the island model, and is given a new value, α_1.

Once again three energy levels and the associated molecular orbitals separate out from the n-fold degenerate system. The characteristic polynomial now becomes

$$P_n = P_n + 2e\,p^{n-1} \qquad -(40)$$

where $e = (\alpha_1-\alpha)(x+\alpha)/(x+\alpha_1)$ -(41)

and $p(x)$ has the form (35). Since $\gamma = 0$, $P_n = p^n$, as before. Therefore

$$P_n = p^{n-1}(p+2e) \qquad -(42)$$

which again means that the n-fold degeneracy is reduced to (n-1) fold degeneracy in the same three roots, and three new single roots are given by

$$p(x) + 2e(x) = 0 \qquad -(43)$$

leading to the cubic equation

$$x^3+(\alpha+\alpha_1)x^2 + (\alpha\alpha_1-4)x - 2\alpha_1 - 2\alpha = 0 \qquad -(44)$$

which may be solved numerically for the three values of x.

6.3.2(b) $P(d_{xz})$

If, instead, a single $P(d_{xz})$ coulomb integral is modified to a value α_2, all other $P(d_{xz})$ and $P(d_{yz})$ coulomb integrals remaining equal to α, the characteristic polynomial becomes

$$P'_n = P_n + 2\,f\,p^{n-1} \qquad -(45)$$

where

$$f = (\alpha_2-\alpha)(x+\alpha)/(x+\alpha_2) \qquad -(46)$$

Again, because $P_n = p^n$, there is (n-1)-fold degeneracy in the original repeated roots and the three new single roots are given by

$$x^3 + (\alpha+\alpha_2)x^2 + (\alpha\alpha_2-4)x - 2\alpha_2 - 2\alpha = 0 \qquad -(47)$$

Comparing (47) with (44) it can be seen that, in the island model where P(d_{yz}) and P(d_{xz}) orbitals participate on an equal footing, an equivalent modification to a single coulomb integral of either kind of orbital leads to a similar effect in terms of the resultant energy levels. The molecular orbitals which separate out are localised within the pair of islands sharing the atomic orbital whose coulomb integral has been modified. The form (22) and its sum and difference companions apply when changes are made in a single α_{yz} value, whereas (23) and its companions apply when single α_{xz} values are modified. Group orbitals for two islands are, therefore, zeroth-order functions for modifications of coulomb integrals of phosphorus atoms.

In contrast to the more widespread effect on energy levels, molecular orbitals, charge densities and bond orders etc., found when a single coulomb integral is modified in a classical p -p system, the effects are here confined wholly to the island or pair of islands associated with the modification, and quantities relating to other parts of the PN framework are unaffected. The island model has significance, therefore, in demonstrating that electrical effects can be localised, in spite of the fact that conjugation extends throughout the entire framework.

6.3.3 Variation of All Coulomb Integrals of One Kind

When all coulomb integrals associated with all the atomic orbitals of one kind are changed by the same amount from the uniform value α, symmetry orbitals represent the appropriate zeroth-order description.

Using the general algebraic solution of section 6.5 it is possible to examine analytically the effects of progressive and uniform increases in (a) all α_{yz} and (b) all α_{xz} values. As the increases become large, the effect is to diminish the participation in conjugation of first the P(d_{yz}) orbitals, and second the P(d_{yz}) orbitals. The results deribed for $(PN)_3$ in the following sub-sections can be seen to provide a formal link with (a) Craig and Paddock's model, and (b) the solution for benzene.

6.3.3(a) Variation of all α_{yz} in $(PN)_3$

The general solution for $(PN)_3$ in section 6.5.2 has the form

$$P_3 \equiv (p-\gamma)^2(p+2\gamma) = 0$$

The cubic factors may be usefully written

$$(p-\gamma) = x^3-4x + \alpha_1(x^2-3) + \alpha_2(x^2-1) + \alpha_1\alpha_2 x \qquad -(48)$$

$$\text{and} \quad (p+2\gamma) = x^3-4x + \alpha_1 x^2 + \alpha_2(x^2-4) + \alpha_1\alpha_2 x \qquad -(49)$$

If $\alpha_2(\neq 0)$ remains small compared with the increasing α_1, the terms of (48) and (49) which involve α_1 dominate when the roots x are small. Thus $(p-\gamma)$ is dominated by the quadratic $(x^2+\alpha_2 x-3)$ and $(p+2\gamma)$ by $(x^2+\alpha_2 x)$, giving rise respectively to roots

$$x = \frac{-\alpha_2 \pm \sqrt{12+\alpha_2^2}}{2} \quad \text{(twice)}$$

$$\text{and} \quad x = 0, -\alpha_2 \qquad -(50)$$

For large values of α_1, the expressions $(p-\gamma) = 0$ and $(p+2\gamma) = 0$ are also satisfied approximately by $x = -\alpha_1$ since under this condition both expressions are dominated by $(x^3+\alpha_1 x^2)$. So, in addition to the roots (50), three further roots $x = -\alpha_1$ occur to complete the set.

Consider now the special case with $\alpha_2 = 0$. When α_1 is also equal to zero, it may be seen from (48) and (49) that the three roots $x = \pm 2, 0$ occur with triple degeneracy. As α_1 is increased, the dominating factors become (x^2-3) and x^2 in $(p-\gamma)$ and $(p+2\gamma)$ respectively. In the limit when the $P(d_{yz})$ orbitals no longer participate, the roots are, therefore,

$$x = \pm\sqrt{3} \text{ (twice) and } x = 0 \text{ (twice)} \qquad -(51)$$

These correspond to the values found by Craig and Paddock who considered only $P(d_{xz})$ and $N(p_z)$ orbitals from the outset. As α_1 increases, the three energy levels corresponding to $x = -\alpha_1$ emerge from above the band enclosing the remaining levels. These are associated with molecular orbitals which are increasingly similar to group orbitals.

6.3.3(b) Variation of all α_{xz} in $(PN)_3$

$P(d_{yz})$ orbital participation in conjugation can be diminished in a similar manner by progressively and uniformly increasing all the α_{xz} values.

Examination of the cubic factors $(p-\gamma)$ and $(p+2\gamma)$, given in (48) and (49), shows that if $\alpha_1 (\neq 0)$ remains small compared with the increasing α_2, then the dominant terms for small roots x are $(x^2+\alpha_1 x-1)$ and $(x^2+\alpha_1 x-4)$ in the two factors respectively. These give rise to roots

$$x = \frac{-\alpha_1 \pm \sqrt{4+\alpha_1^2}}{2} \text{ (twice) and } x = \frac{-\alpha_1 \pm \sqrt{16+\alpha_1^2}}{2} \qquad -(52)$$

For large values of α_2, three further roots, given by $x \doteqdot -\alpha_2$, complete the set.

In the special situation with $\alpha_1 = 0$, the roots tend to the limits

$$x = \pm 1 \text{ (twice)}, \quad x = \pm 2 \qquad -(53)$$

as α_2 becomes large and the $P(d_{xz})$ orbitals are taken out of conjugation. Thus the remaining $P(d_{yz})$ and $N(p_z)$ orbitals participate in conjugation which increasingly resembles in character the conjugation found for benzene. The 'benzene-like' symmetry orbitals corresponding to $x = \pm 2$ remain unchanged throughout the process. Once more, three energy levels, corresponding to $x = -\alpha_2$, emerge above the band, and the related molecular orbitals tend towards localised $P_3(d_{xz})$ group orbitals as α_2 becomes large.

6.4 Linear PN Systems

For the case $\alpha_1 = \alpha_2 = 0$, applied to cyclic systems, the charge densities are given by

$$q_n = 1.0 \, , \; q_p\,(d_{yz}) = 0.5, \; q_p(d_{xz}) = 0.5 \qquad -(54)$$

and the bond orders are of modulus unity, but 'shared' between d_{xz}-p_z (= ±0.5) and d_{yz}-p_z (= +0.5).

The characteristic polynomial for the $(PN)_n$ linear system, with $\alpha_1 = \alpha_2 = 0$, may be derived from the general analytical forms given in section 6.5.4.

i.e. $\quad P_n' = p' \, p^{n-1} \qquad -(55)$

where $\quad p' = p + 2x \qquad -(56)$

So, in addition to the (n-1) fold degeneracy in similar roots (±2,0) to those found for the cyclic systems, there are three single roots, arising from $p'(x) = 0$.

These are

$$x = 0 \quad , \quad x = \pm\sqrt{2} \qquad -(57)$$

and are associated with the 'end effects'. The roots can be related to the solution for the cyclic system, and particularly to the idea that the linear system can be obtained from the cyclic system by breaking a bond in the island model. It may be assumed, for example, that the bond joining atoms $P^{(1,2)}$ and $N^{(3n)}$ of the cyclic system shown in figure 6.1 is the one to be broken. Then, whereas the 'first' island, $\{\phi_i ; i = 1,2,\ldots,5\}$ is complete, the 'final' island, $\{\phi_i ; i = 3_n-2, 3_n-1, 3_n\}$ is incomplete and gives rise to the roots $\pm\sqrt{2}$, 0, found earlier.

The charge distribution in the two terminal islands is also changed, since although the atomic charge densities are unity elsewhere, within the terminal islands

$$q_1 (d_{yz}) = q_2(d_{xz}) = 0.25$$

and

$$q_{3n-2} (d_{yz}) = q_{3n-1} (d_{xz}) = 0.75$$

Thus π electron charge is effectively transferred from $P^{(1,2)}$ to $P^{(3n-2,\ 3n-1)}$ by the breaking of the bond.

6.5 A General Algebraic Solution

In this section a general algebraic solution of the Huckel equations for PN ring systems, together with some results derived from the solution, will be given. Initially, no restrictions are placed upon the values of the five parameters α_{yz}, α_{xz}, α_z, β_1 and β_2, defined as follows

$$\alpha_{yz} = \alpha_o + \alpha_1 \beta$$

$$\alpha_{xz} = \alpha_o + \alpha_2 \beta$$

$$\alpha_z = \alpha_o + \alpha_3 \beta$$

$$\langle d_{yz}|h|p_z\rangle = \beta_1 = k_1 \beta$$

$$\langle d_{xz}|h|p_z\rangle = \beta_2 = k_2 \beta$$

with α_o as an arbitrary chosen origin and β as the unit of energy.

When the customary substitution $x = (\alpha_o - \varepsilon)/\beta$ is made the determinantal equation expressing the condition for non-trivial solutions takes the form.

$$\begin{vmatrix} E & K & 0 & 0 & \cdots & K' \\ K' & E & K & 0 & \cdots & 0 \\ 0 & K' & E & K & \cdots & 0 \\ 0 & & K' & E & \cdots & 0 \\ & & & & E & K \\ K & 0 & 0 & 0 & K' & E \end{vmatrix} = 0 \qquad -(1)$$

where E and K are, respectively, the matrices

$$\begin{bmatrix} \alpha_1+x & 0 & k \\ 0 & \alpha_2+x & -k_2 \\ k_1 & -k_2 & \alpha_3+x \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ k_1 & k_2 & 0 \end{bmatrix} \qquad -(2)$$

K' is the transpose of K and, within the determinant of (1), O represents the 3 by 3 null matrix.

The ordering of the elements in (2) corresponds to a scheme where the $P(d_{yz})$ orbitals are numbered 1,4,7,..., the $P(d_{xz})$ are numbered 2,5,8,..., and the $N(p_z)$ are numbered 3,6,9,...etc.

By making use of standard row and column manipulations, the determinantal equation (1) can be re-expressed as

$$P_n \equiv \begin{vmatrix} N & A & 0 & 0 & \cdots & A \\ A & N & A & 0 & \cdots & 0 \\ 0 & A & N & A & \cdots & 0 \\ 0 & 0 & A & N & \cdots & 0 \\ & & & \cdots & N & A \\ A & 0 & 0 & 0 \cdots & A & N \end{vmatrix} = 0 \qquad -(3)$$

where N and A are, respectively, the matrices

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & p \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \gamma \end{bmatrix} \qquad -(4)$$

$$\text{with } p = (x+\alpha_1)(x+\alpha_2)(x+\alpha_3)-2 \quad \beta_1{}^2(x+\alpha_2)+\beta_2{}^2(x+\alpha_1) \qquad -(5)$$

$$\text{and } \gamma = \beta_2{}^2(x+\alpha_1)-\beta_1{}^2(x+\alpha_2) \qquad -(6)$$

Thus $P_n = 0$ is the characteristic equation of order 3n associated with the $(PN)_n$ ring system.

Solutions of special interest may be obtained by assigning particular values to the five parameters involved in equation (3).

6.5.1 $\alpha_1 = \alpha_2$; $\beta_1 = \beta_2$

In this special case all elements of A become zero, since $\gamma = 0$. Thus P_n can be seen to reduce to $p(x)^n$, giving n-fold degeneracy in the three roots of $p(x) = 0$. It is convenient to reduce the number of symbols involved at this point by setting $\beta_1 = \beta_2 = \beta$, the common resonance integral, so that $k_1 = k_2 = 1$, and by choosing $\alpha_z = \alpha_0$ as the origin of energy, so that α_3 is formally zero. Under these conditions p(x) becomes

$$p(x) = x^3+(\alpha_1+\alpha_2)x^2-(4-\alpha_1\alpha_2)x-2(\alpha_1+\alpha_2) \qquad -(7)$$

and, with $\alpha_1 = \alpha_2 = \alpha$ say, p(x) then factorises to give

$$p(x) = (x+\alpha)(x^2+\alpha x-4) \qquad -(8)$$

and the required roots, represented in figure 6.2, are

$$-\alpha \text{ and } (-\alpha\pm\sqrt{\alpha^2+16})/2 \qquad -(9)$$

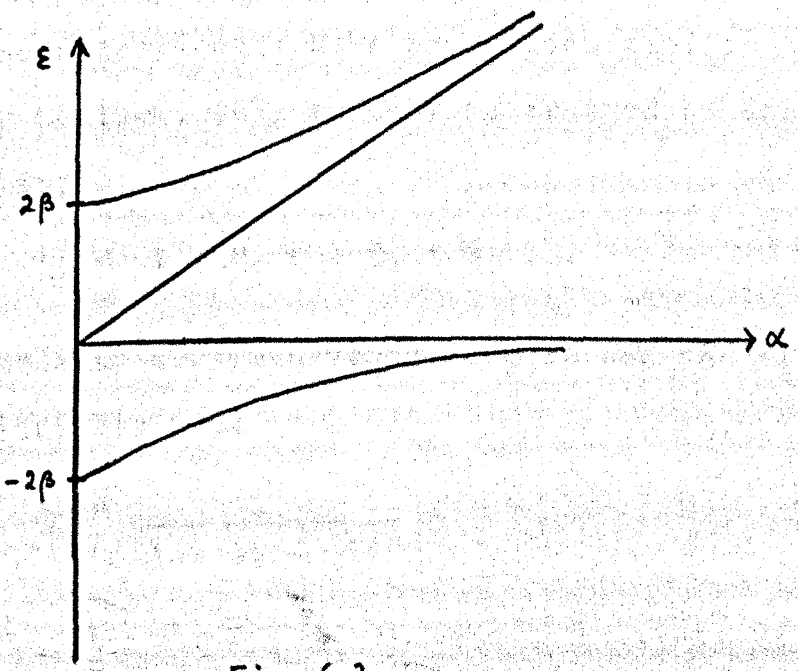


Fig. 6.2.

6.5.2 $\alpha_1 \neq \alpha_2$

Consider determinants having the form

$$D_n \equiv \begin{vmatrix} N & A & 0 & 0 & \cdots & 0 \\ A & N & A & 0 & \cdots & 0 \\ 0 & A & N & A & \cdots & 0 \\ 0 & 0 & A & N & \cdots & 0 \\ \vdots & & & \vdots & & \vdots \\ & & & \cdots & N & A \\ 0 & 0 & 0 & 0 \cdots & A & N \end{vmatrix} \qquad -(10)$$

with N and A being the 3 by 3 matrices as defined earlier in (4).

The determinants D_n may be expanded to give

$$D_1 = p$$
$$D_2 = p^2 - \gamma^2$$
$$D_3 = p^3 - 2\gamma^2 p$$

and a recurrence formula $D_n = pD_{n-1} - \gamma^2 D_{n-2}$ -(11)

where D_o is equal to 1.

These determinants have properties similar to those described by Coulson, {6}, and may be treated as follows -

Writing

$$\Delta = 1 + D_1 t + D_2 t^2 + \ldots \qquad -(12)$$

and noting that the recurrence formula and the first few values of (12) indicate that

$$\Delta = \frac{1}{1 - pt + \gamma^2 t^2} \qquad -(13)$$

Putting $p = 2\gamma \cos\theta$ and equating coefficients of t^r in the partial fraction form of Δ, leads to the result

$$D_n = \gamma^n \frac{\sin(n+1)\theta}{\sin\theta} \qquad -(14)$$

Now, expanding the modified Huckel determinants P_n, given in (3), by rows gives

$$P_n = pD_{n-1} - 2\gamma^2(D_{n-2} - (-1)^n\gamma^{n-2})$$

$$= D_n - \gamma^2 D_{n-2} - 2(-\gamma)^n \qquad -(15)$$

Finally, conversion of D_n and D_{n-2} to trigonometrical form, using (14), yields

$$P_n = 2\gamma^n \left\{\cos n\theta - (-1)^n\right\} \qquad -(16)$$

Thus it is possible to obtain the individual P_n in a compact form -

e.g. $P_3 = (p-\gamma)^2(p+2\gamma)$

$P_4 = (p-2\gamma)p^2(p+2\gamma)$

$P_5 = (p^2-\gamma p-\gamma^2)^2(p+2\gamma)$

$P_6 = (p-2\gamma)(p-\gamma)^2(p+\gamma)^2(p+2\gamma)$ -(17)

and so on.

The form of a general solution for $\alpha_1 \neq \alpha_2$ $\beta_1 \neq \beta_2$ can be understood qualitatively from these results. However, for simplicity, consider in the first instance the case $\beta_1 = \beta_2$ with $\gamma = \alpha_1 - \alpha_2$. Imagine a line, $\gamma^* =$ constant moving parallel to the x axis through the cubic p(x), thereby giving roots of

$P_n(x) = 0$ at $\gamma^* = \gamma, -2\gamma$ and so on.

The relative positioning of the energy levels of P_3, for example, may be seen in this way from figure 6.3

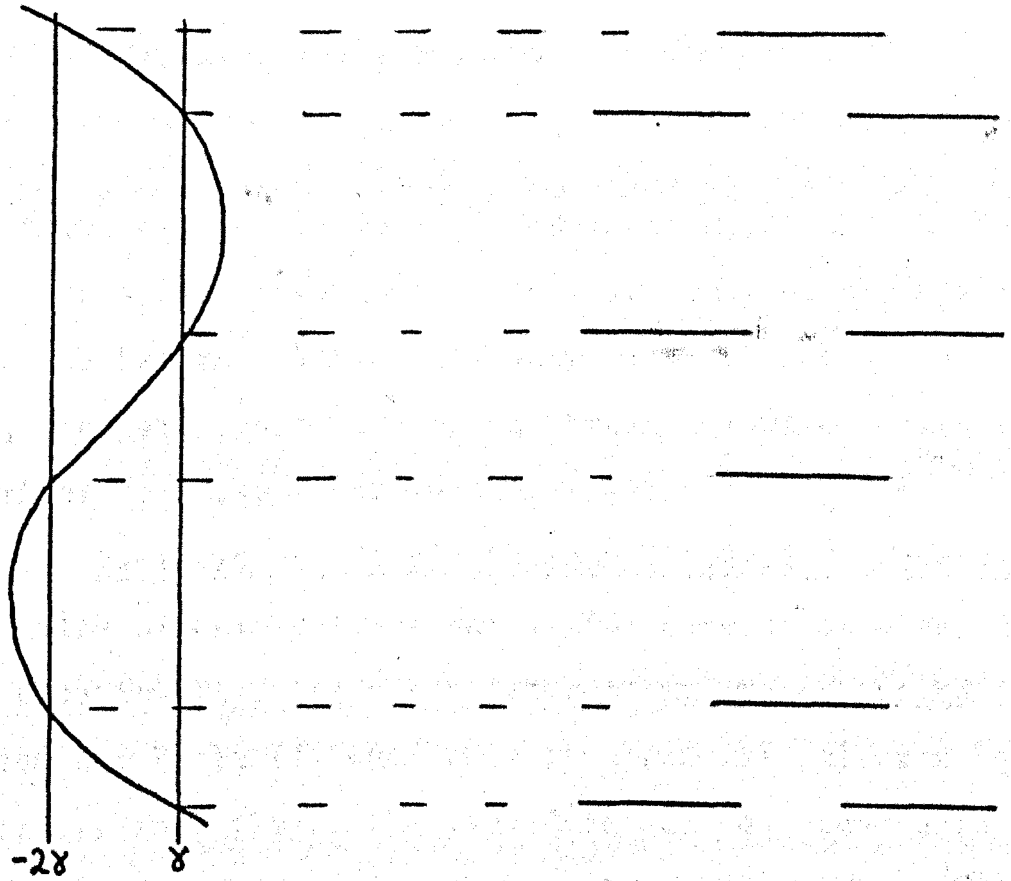


Fig. 6.3

It follows from equation (16), as exemplified in (17), that the lowest levels for odd n are doubly degenerate, being associated with a squared term in every instance. Similarly it can be seen that for even n the lowest level is always single. The highest energy level in all cases is single, with a common value for all n.

The general solution of the determinantal equation for $(PN)_n$ cyclic systems is characterised by a combination of sets of single and doubly degenerate levels. Under the condition

$\gamma = \alpha_1 - \alpha_2 = 0$, these levels collapse into the triply degenerate scheme.

In the general case where $\beta_1 \neq \beta_2$, the parameter γ is given by

$$\gamma = \beta_2^2(x+\alpha_1) - \beta_1^2(x+\alpha_2) \qquad -(18)$$

which represents a straight line of gradient $(\beta_2^2 - \beta_1^2)$. The spectrum may now be interpreted in terms of the intersections of such a line moving with constant gradient through the cubic p(x) as before. Subject to only minor variation between β_1 and β_2, the patterns of levels so obtained remain substantially similar to those found when $\beta_1 = \beta_2$.

6.5.3 Variation of Single Coulomb Integrals - General Results

The algebraic treatment of the general problem, described by equation (1), leads via determinant operations to the expression for P_n in (3) and hence to a general solution in trigonometrical form (16). The procedure may be extended to take account of modifications to any single coulomb integral in the cyclic system.

Such a modification corresponds to a change in one of the parameters α_1, α_2 or α_3 belonging to just one of the matrices E appearing in the determinantal equation (1). Without loss of generality the change may, for analytical convenience, be regarded as taking place within the matrix E which stands in the first position of the leading diagonal in the determinant of (1).

In the following sub-sections, single coulomb parameters associated with $N(p_z)$, $P(d_{yz})$ and $P(d_{xz})$ will be modified in turn, and the consequent variations in the general solution will be derived and analysed. In each instance it will be seen that the characteristic polynomial P_n is modified by the addition of a term Δ_n. This extra term is found to always possess certain factors in common with P_n. Consequently it is possible to identify those roots of $P_n = 0$ which remain unchanged as a result of the modification, and to determine the new roots arising from the equation $P_n' = 0$.

6.5.3(a) $N(p_z)$

Suppose the single α_3 in the matrix E identified above is changed to a value α_3 by the addition of a quantity $\delta\alpha_3$, so that

$$\alpha_3' = \alpha_3 + \delta\alpha_3 .$$

The same determinant manipulations as were previously carried out for the unperturbed system lead, in this case, to a form corresponding to (3) but with the single leading matrix N replaced by N'. N' itself differs from N by the replacement of p with p' where

$$p' = p + \delta\alpha_3 \ (x+\alpha_1)(x+\alpha_2) \qquad -(19)$$

The modified characteristic polynomial P_n' is therefore obtained in the form

$$P_n' = P_n + \Delta_n^z$$

where

$$\Delta_n^z = d'D_{n-1} \quad \text{with } d' = \delta\alpha_3 \ (x+\alpha_1)(x+\alpha_2) \qquad -(20)$$

Using expression (14), the term Δ_n^z may be expressed in trigonometrical form, giving

$$\Delta_n^z = d'\gamma^{n-1}\frac{\sin n\theta}{\sin\theta} \qquad -(21)$$

where γ is defined in (6) and $\theta = \cos^{-1}(p/2\gamma)$ as in 6.5.2.

The table below gives the factors in P_n and Δ_n^z/d' for the first few values of n.

n	P_n	Δ_n^z/d'
3	$(p-\gamma)^2(p+2\gamma)$	$(p-\gamma)(p+\gamma)$
4	$(p-2\gamma)p^2(p+2\gamma)$	$(p^2-2\gamma^2)p$
5	$(p^2-\gamma p-\gamma^2)^2(p+2\gamma)$	$(p^2-\gamma p-\gamma^2)(p^2+\gamma p-\gamma^2)$
6	$(p-2\gamma)(p-\gamma)^2(p+\gamma)^2(p+2\gamma)$	$(p^2-3\gamma^2)(p-\gamma)p(p+\gamma)$

From these results it can be seen that in the general case ($\gamma \neq 0$), the only roots retained as $P_n \to P_n + \Delta_n^z = P_n'$ will be those arising out of the repeated factors of P_n, but the equivalent energy levels will occur singly in the modified system.

6.5.3(b) $P(d_{yz})$

Suppose now that the single α_1 in the leading matrix E of (1) is modified so that

$$\alpha_1' = \alpha_1 + \delta\alpha_1$$

Determinant manipulations now lead to a slightly different expression for P_n', corresponding to (3).

Here

$$P_n' = \begin{vmatrix} N' & A & 0 & \cdots & 0 & A' \\ A & N & A & \cdots & 0 & 0 \\ 0 & A & N & & & \\ \vdots & & & & & \vdots \\ 0 & 0 & & & N & A \\ A & 0 & & \cdots & A & N' \end{vmatrix} \qquad -(22)$$

where N and A are as defined in (4) but where N' and A' are, respectively, the matrices

$$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \gamma+e' \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & p+e' \end{bmatrix} \qquad -(23)$$

with $e' = \delta\alpha_1 \dfrac{(x+\alpha_2)}{(x+\alpha_1')}$

P_n' can be manipulated into the form

$$P_n' = P_n + \Delta_n^{yz}$$

where

$$\Delta_n^{yz} = 2e' \, (D_{n-1} - F_{n-1}) \qquad -(24)$$

with D_n as defined earlier and with the determinant F_n obtained by replacing the n^{th} column of the determinant form of D_n, given in (10), by the transpose of

$$(0,0,\gamma,0,\ldots,0,0,\gamma)$$

F_n may be expanded to give a suitable expression for F_{n-1},

$$F_{n-1} = \gamma\ (D_{n-2} + (-\gamma)^{n-2}) \qquad -(25)$$

giving

$$\Delta_n^{yz} = 2e'\ (D_{n-1} - \gamma D_{n-2} + (-\gamma)^{n-1}) \qquad -(26)$$

which may also be expressed in trigonometrical form as

$$\Delta_n^{yz} = 2e'\gamma^{n-1}\ \frac{\cos(n-\frac{1}{2})\theta}{\cos\theta/2} + (-1)^{n-1} \qquad -(27)$$

The table below gives the factors of P_n and $\Delta_n^{yz}/2e'$ for the first few values of n

n	P_n	$\Delta_n^{yz}/2e'$
3	$(p-\gamma)^2(p+2\gamma)$	$p(p-\gamma)$
4	$(p-2\gamma)p^2(p+2\gamma)$	$p(p-2\gamma)(p+\gamma)$
5	$(p^2-\gamma p-\gamma^2)^2(p+2\gamma)$	$(p^2-\gamma p-\gamma^2)(p^2-2\gamma^2)$
6	$(p-2\gamma)(p-\gamma)^2(p+\gamma)^2(p+2\gamma)$	$(p-2\gamma)(p-\gamma)(p+\gamma)(p^2+\gamma p-\gamma^2)$

Thus the roots corresponding to the lowest factor of P_n are retained as $P_n \rightarrow P_n + \Delta_n^{yz} = P_n'$, together with sets of single roots equal in value to the repeated roots of $P_n = 0$.

6.5.3(c)

If α_2 is now modified in the leading matrix E of (1), so that

$$\alpha_2' = \alpha_2 + \delta\alpha_2,$$

the determinant manipulations lead to the expression (22) once again, but where N' and A' are, respectively, the matrices

$$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & p+f' \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \gamma-f' \end{bmatrix} \qquad -(28)$$

with

$$f' = \delta\alpha_2 \frac{(x+\alpha_1)}{(x+\alpha_2')}$$

P_n' may be obtained in the form

$$P_n' = P_n + \Delta_n^{xz}$$

where

$$\Delta_n^{xz} = 2f'(D_{n-1} + F_{n-1}) \qquad -(29 \qquad -(29)$$

or, in trigonometrical form

$$\Delta_n^{xz} = 2f'\gamma^{n-1} \frac{\sin(n-\frac{1}{2})\theta}{\sin\theta/2} - (-1)^{n-1} \qquad -(30)$$

the table below gives the factors of P_n and $\Delta_n^{xz}/2f'$ for the first few values of n

n	P_n	$\Delta_n^{xz}/2f'$
3	$(p-\gamma)^2(p+2\gamma)$	$(p-\gamma)(p+2\gamma)$
4	$(p-2\gamma)p^2(p+2\gamma)$	$(p-\gamma)p(p+2\gamma)$
5	$(p^2-\gamma p-\gamma^2)^2(p+2\gamma)$	$(p^2-\gamma p-\gamma^2)p(p+2\gamma)$
6	$(p-2\gamma)(p-\gamma)^2(p+\gamma)^2(p+2\gamma)$	$(p-\gamma)(p+\gamma)(p^2-\gamma p-\gamma^2)(p+2\gamma)$

Thus the roots corresponding to the highest factor of P_n are retained as $P_n \to P_n + \Delta_n^{xz} = P_n'$, together with single roots equal in value to the repeated roots of $P_n = 0$.

The factors given in the three tables above may be derived, as may similar results for larger values of n, by finding the values of θ which make Δ_n^z, Δ_n^{yz} and Δ_n^{xz} equal to zero. These are given in the table below, together for comparison with those which satisfy $P_n = 0$.

	θ	
	n odd	n even
P_n	$\frac{2r+1}{n}\pi$	$\frac{2r}{n}\pi$
Δ_n^z	$\frac{r+1}{n}\pi$	$\frac{r+1}{n}\pi$
Δ_n^{yz}	$\frac{2r+1}{n}\pi$	$\frac{2r}{n}\pi$
	$\frac{2r+1}{n-1}\pi$	$\frac{2r+2}{n-1}\pi$
Δ_n^{xz}	$\frac{2r+1}{n}\pi$	$\frac{2r+2}{n}\pi$
	$\frac{2r+2}{n}\pi$	$\frac{4r+1}{n-1}\pi$

In each case r runs from 0,1,... etc. The first n values of θ are to be used when finding P_n and the first n-1 values are relevant in the case of each Δ term.

Thus, for example, P has zeros at

$$\theta = 0, \frac{\pi}{3}, \frac{2\pi}{3}, \pi, \frac{4\pi}{3}, \frac{5\pi}{3}$$

i.e. when $p(=2\gamma\cos\theta)$ is given by

$$p = 2\gamma, \gamma, -\gamma, -2\gamma, -\gamma, \gamma$$

Therefore $P_6 = (p-2\gamma)(p-\gamma)^2(p+\gamma)^2(p+2\gamma)$, as given earlier.

Similarly Δ_6^{yz} has zeros at

$$\theta = 0, \frac{\pi}{3}, \frac{2\pi}{5}, \frac{2\pi}{3}, \frac{4\pi}{5}$$, leading to

$$\Delta_6^{yz} = (p-2\gamma)(p-\gamma)(p+\gamma)(p^2+\gamma p-\gamma^2)$$, as before.

6.5.4 Linear $(PN)_n$ Systems - General Solution

The determinantal equation arising in the analysis of linear structures is the same as that in (1) except for the elements K' and K appearing in the final position of the first row and in the first position of the final row, respectively. Each is replaced by the 3 by 3 null matrix 0. The determinant may be manipulated into a form corresponding to (3). In fact the resulting determinant is identical with D_n except for the first term of the leading diagonal in which N' replaces N, where

$$N' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & p' \end{bmatrix} \qquad -(31)$$

with $$p' = p + \beta_1^2 (x+\alpha_2)+\beta_2^2 (x+\alpha_1) \qquad -(32)$$

where p is given in (5).

Expansion leads to a general form for the characteristic polynomial P_n^L

$$\text{i.e.} \quad P_n^L = p'D_{n-1} - \gamma^2 D_{n-2} \qquad -(33)$$

where D_n is defined in (11) and γ is given in (6).

In general P_n^L will have some roots in common with P_n only when $\gamma = 0$.

If $\alpha_1 = \alpha_2$ and $\beta_1 = \beta_2$, $P_n^L = p'D_{n-1} = p'p^{n-1}$, leading to (n-1)-fold degeneracy in the roots of p(x), given in (9), together with three additional single roots arising from

$$p'(x) = 0$$

6.6 References

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CHAPTER SEVEN

d_{π}-p_{π} BONDING IN PHOSPHONITRILIC COMPOUNDS - THE SCF-CI METHOD

This chapter continues the investigation into d_{π}-p_{π} bonding, which began with the analysis of solutions derived within the Huckel approximation, given in the previous chapter.

The investigation now proceeds within the framework of the SCF-CI method, and concentrates on developing the interesting and important concept of island orbitals which arose out of solutions of the Huckel model for PN systems.

The Huckel molecular orbital method, being a nearest neighbour approximation, does not explicitly allow for interactions between island orbitals. Such interactions would be indicated by the appearance of off-diagonal elements in the hamiltonian matrix expanded in a basis of island orbitals, and the existence of these elements could produce a delocalisation effect. Thus the island orbital solutions obtained using the Huckel method might simply be a fortuitous but misleading outcome of the form of approximation adopted.

This is the reason for undertaking further investigations using the SCF method. The SCF matrix explicitly includes interaction terms, and these could be expected to lead to delocalisation effects throughout the system. In fact, island orbitals will be shown to persist, under certain conditions, as solutions to the SCF equations.

The investigation described in this chapter has been firmly based upon the computational approach, whereby computer solutions to theoretical models are found for a variety of given parameter values, and are then used along with numerical and graphical techniques to identify properties of the solutions which, in turn, assist in a theoretical study of the model itself.

Using this type of approach, a closed form expression for the SCF island orbitals has been found. It has enabled a short computer program to be written for finding island orbitals in numerical form much more quickly, and using far less computer storage, than the equivalent conventional SCF computation. The ready availability of such solutions has made possible an extensive numerical study of the properties of CI solutions, and the results obtained have been used to assist in a theoretical study at this level.

On the strength of evidence thus obtained, it is possible to arrive at conclusions regarding the influence of the island orbital solution on the UV spectrum. This question is discussed in the final section of the chapter.

Hence, beginning with the Huckel computer calculations, and leading ultimately to theoretical conclusions concerning CI solutions, this repeated sequence of computer calculations followed by theoretical deductions, demonstrates the power of the computational approach in both seeking out and formally establishing the properties of theoretical models.

7.1 The SCF Method

The complete investigation using the SCF-CI method comprises the sequence of computer experiments and theoretical deductions described above. The description which follows is presented in the same sequence, with the SCF method first of all treated separately from the CI method.

7.1.1 The SCF Equations

The SCF equations for π electron systems, using the P-P-P approximation, were given in chapter two, and may be written

$$\sum_{\nu} h_{\mu\nu}\, c_{\nu i} = \varepsilon_i\, c_{\mu i} \quad , \qquad -(1)$$

$$h_{\mu\mu} = \omega_{\mu} + \tfrac{1}{2}P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\nu\neq\mu}(P_{\nu\nu}-Z_{\nu})\gamma_{\mu\nu} \quad , \qquad -(2)$$

$$h_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \quad , \qquad -(3)$$

$$P_{\mu\nu} = 2\sum_{k} c_{k\mu}c_{k\nu} \qquad -(4)$$

$$\gamma_{\mu\nu} = (\mu\mu|\nu\nu) \qquad -(5)$$

where Z_{ν} is the effective, screened, charge at the framework ion ν,

ω_{μ} and $\beta_{\mu\nu}$ are, respectively, diagonal and off-diagonal elements of the core framework hamiltonian,

h is the 'effective' hamiltonian,

ε_i and $\underline{c_i}$ are corresponding eigenvalues and eigenvectors of h,

P is the bond order matrix, involving a summation over occupied orbitals k,

$\gamma_{\mu\nu}$ is the electron repulsion integral.

In order to make it easier to compare solutions of the SCF equations with those obtained using the Huckel method, and also to effect a comparison with SCF solutions for alternant hydrocarbons, the diagonal terms (2) were once more modified by subtracting from each the term

$$\omega + \tfrac{1}{2}\gamma \qquad -(6)$$

which represents the leading terms of (2) particularised for carbon atoms.

As a result, the SCF diagonal term, corresponding to the Huckel coulomb parameter, may be written

$$\alpha_{\mu} = \delta\omega_{\mu} + \tfrac{1}{2}(P_{\mu\mu}\gamma_{\mu\mu}-\gamma) + \sum_{\nu\neq\mu} (P_{\nu\nu}-Z_{\nu})\gamma_{\mu\nu} \qquad -(7)$$

where $\delta\omega_{\mu} = \omega_{\mu}-\omega$.

Special account must be taken of the fact that there are two d-orbitals on each Phosphorus atom, and just one p-orbital on each Nitrogen atom of the P-N system. Separate equations, equivalent to (2), can be derived from the general expression given in chapter two, for each diagonal element in the SCF matrix within the P-P-P approximation. Written in a form corresponding to (7), these are

$$\alpha_{\mu}^{P} = \delta\omega_{\mu}^{P} + \tfrac{1}{2}(P_{\mu\mu}\gamma_{\mu\mu}-\gamma) + \tfrac{1}{2}P_{\mu\mu'}\gamma_{\mu\mu'}$$

$$+ \sum_{\substack{P \\ \lambda\neq\mu \\ \lambda\neq\mu'}} (P_{\lambda\lambda}+P_{\lambda'\lambda'}-Z_{\lambda})\gamma_{\mu\lambda} + \sum_{\substack{N \\ \sigma\neq\mu}} (P_{\sigma\sigma}-Z_{\sigma})\gamma_{\mu\sigma} \qquad -(8)$$

$$\alpha_{\nu}^{N} = \delta\omega_{\mu}^{N} + \tfrac{1}{2}(P_{\mu\mu}\gamma_{\mu\mu}-\gamma)$$

$$+ \sum_{\substack{P \\ \lambda\neq\nu}} (P_{\lambda\lambda}+P_{\lambda'\lambda'}-Z_{\lambda})\gamma_{\nu\lambda} + \sum_{\substack{N \\ \sigma\neq\nu}} (P_{\sigma\sigma}-Z_{\sigma})\gamma_{\nu\sigma} \qquad -(9)$$

α_{μ}^{P} refers to any Phosphorus d-orbital and α_{ν}^{N} to Nitrogen p-orbitals. μ,μ' and λ,λ' refer to pairs of d-orbitals on the same P atom, and the summations Σ_P and Σ_N are taken over all P and N atoms, respectively.

In (8), the term $(P_{\lambda\lambda}+P_{\lambda\lambda'}-Z_{\lambda})\gamma_{\mu\lambda}$ represents the potential at μ due to the effective net charge at P atom λ. The summations in (8) give, therefore, the total potential at μ due to the net charges at all the other P atoms and at all of the N atoms. Similar interpretations may be given to the summations in (9). The term $\frac{1}{2} P_{\mu'\mu'}\gamma_{\mu\mu'}$ in the expression (8) for α_{μ}^{P} is an extra potential accounted for by interaction with the π-electron charge density $P_{\mu'\mu'}$ associated with the companion d-orbital.

7.1.2 Numerical Study of the SCF Solutions

The SCF equations (1) were initially solved numerically using the standard iterative procedure. The core hamiltonian formed the first 'estimate' of the SCF matrix h, and this was diagonalised to give a set of $\underline{c_i}$ which were used in (4) to give the P matrix required by (3), (8) and (9). These expressions specify the new h, and the process was repeated until self-consistency was attained in the $\underline{c_i}$.

Parameter schemes for $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ resembling those used in the P-P-P method applied to hydrocarbons were adopted here, since the aim was not to attempt to re-produce accurate solutions as compared with experiment, but rather simply to examine properties of the equations and their solutions. In any case, the analysis led eventually to a general solution in terms of algebraically expressed parameters, which can be analysed for any given parameter values.

For consistency, the integral $\gamma_{\mu\mu'}$ was set equal to the value given to $\gamma_{\mu\mu}$ which, in the first instance, was γ for all μ, and Z=1 for each atom.

First of all an attempt was made to produce conditions for obtaining island orbitals in the SCF approximation by setting all parameters $\delta\omega_\mu$ equal to zero, and by letting $\beta_{\mu\nu} = \pm\beta$ for neighbouring μ and ν, as in the Huckel case. Knowing from the Huckel solution that the resultant charge density should, under these conditions, be uniform around the ring with

$$q_{dyz} = q_{dxz} = 0.5 \ , \quad q_{pz} = 1.0 \quad , \qquad -(10)$$

it was expected that α_μ^P and α_μ^N, given in (8) and (9), would be zero and that a solution analagous to the Huckel solution, with energy levels symmetrically distributed about zero would be obtained.

Computer solutions were found for $(PN)_n$, with n = 3,4,5 and 6, and were observed to possess the properties

(a) (i) n-fold degeneracy in three energy levels, but the energies were not constant with respect to n,

(ii) The three energies were all non-zero and were not distributed symmetrically,

(iii) Apparently delocalised MO's (but islands were not expected to emerge directly from the computer solution),

(iv) MO's associated with central orbital energy were confined to P atoms, as in Huckel case,

(v) Charge density not evenly distributed between P and N atoms, but

$$q_{dyz} = q_{dxz} \ , \text{ and } q_{dyz} + d_{dxz} + q_{pz} = 2 \qquad -(11)$$

(vi) Charge densities at individual atoms varied with n,

(vii) At each iteration the relationship

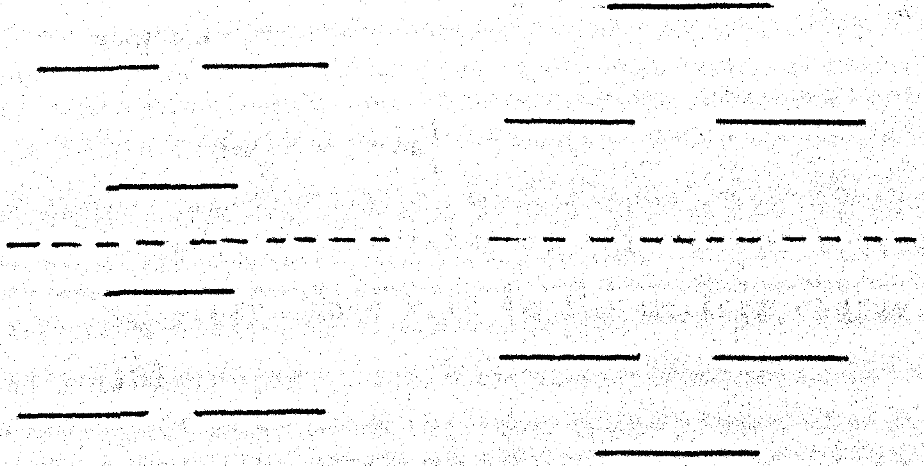
$$\alpha_{\mu}^{P} = \alpha_{\mu'}^{P} = -\alpha_{\nu}^{N} \qquad -(12)$$

was maintained by the diagonal terms of the SCF matrix.

Before commencing a theoretical study of the model and the solutions, some further numerical experiments were carried out on $(PN)_3$. These will now be described, together with observations based on the results obtained.

(b) (i) All $\delta\omega_{\mu}^{P}$ for just d_{yz} orbitals were uniformly and progressively increased, giving solutions comparable with those found in similar numerical experiments with the Huckel model, and described theoretically in the previous chapter. The energy levels were distributed as shown in figure 7.1(i).

(ii) Next, all $\delta\omega_{\mu}^{P}$ for just d_{xz} orbitals were increased, with the resulting energy level pattern approaching the benzene-like form shown in figure 7.1(ii)



(i) Figure 7.1 (ii)

(c) (i) All $\delta\omega_\nu^N$ were progressively modified over a wide range, with all $\delta\omega_\mu^P$ kept equal to zero. It was found that a particular (negative) value $\overline{\delta\omega}_\nu^N$ gave a solution with the uniform charge distribution (10), and with three triply degenerate energy levels of which the central energy level was at $-2\overline{\delta\omega}_\nu^N$. The SCF matrix diagonal elements were then given by

$$\alpha_\mu^P = \alpha_{\mu'}^P = 0, \qquad \alpha_\mu^N = \delta\overline{\omega}_\nu^N \, . \qquad -(13)$$

(ii) All $\delta\omega_\mu^P$ were modified over a wide range, keeping $\delta\omega_\mu^P = \delta\omega_{\mu'}^P$, and keeping $\delta\omega_\nu^N = 0$. This time a positive value $\overline{\delta\omega}_\mu^P$ was found which gave a uniform charge solution. The highest and lowest of the three triply degenerate energies were symmetrical about zero, and the central energy was given by $2\overline{\delta\omega}_\mu^P$. The SCF matrix diagonal elements were then given by

$$\alpha_\mu^P = \alpha_{\mu'}^P = \overline{\delta\omega}_\mu^P \, , \qquad \alpha_\nu^N = 0 \qquad -(14)$$

(iii) The values $\overline{\delta\omega}_\nu^N$ and $\overline{\delta\omega}_\mu^P$ found in (i) and (ii) were related by

$$\overline{\delta\omega}_\nu^N = -\overline{\delta\omega}_\mu^P \qquad -(15)$$

In fact, a difference of this amount between $\delta\omega_\nu^N$ and $\delta\omega_\mu^P$ always gave rise to the uniform charge solution (10).

(d) Attempts were made to derive, numerically, island orbitals in the same forms as those found using the Huckel method, i.e. for the first five atomic orbitals

$s(\phi_1-\phi_2) \pm t\phi_3 + s(\phi_4+\phi_5)$ -(16)

and $s'(\phi_1-\phi_2) - s'(\phi_4+\phi_5)$ -(17)

with one form for each of the three energy levels, and where s,t,s are non-normalised coefficients of atomic orbitals ϕ_i such that ϕ_1 and ϕ_4, ϕ_2 and ϕ_5 are $P(d_{yz})$ and $P(d_{xz})$ and ϕ_3 is a $N(p_z)$ atomic orbital, respectively.

The procedure was to first combine the computed coefficients for the delocalised MO's by taking sums and differences as suggested by (16) and (17). This is equivalent to changing the basis of atomic orbitals. Next, linear combinations of the three MO's in the new basis corresponding to a single energy were sought, such that true island forms similar to (16) and (17) emerged. In other words an island molecular orbital based on the first five atomic orbitals was required to have the coefficients

$s, -s, \pm t, s, s, 0, 0, 0, 0$ -(18)

or $s', -s', 0, -s', -s', 0, 0, 0, 0$ -(19)

in the original basis of ϕ_i for $(PN)_3$.

The operation proved to be possible for MO's derived from SCF equations modified as described in c(iii) above.

For the original MO's obtained when all $\delta\omega_\mu^P = \delta\omega_\nu^N = 0$, islands could still be found, but in a slightly more general form

$s_1(\phi_1-\phi_2) + t_1\phi_3 + s_1(\phi_4+\phi_5)$ -(20)

$s_2(\phi_1-\phi_2) - t_2\phi_3 + s_2(\phi_4+\phi_5)$ -(21)

and $s'(\phi_1-\phi_2) - s'(\phi_4+\phi_5)$, etc. -(22)

The structure of the SCF matrix and of the bond order matrix were closely noted throughout all the above experiments.

(e) In particular, it was observed that, provided $\delta\omega_{\mu}^{P} = \delta\omega_{\mu'}^{P}$, the SCF matrix was always of the general form

$$X \equiv \begin{bmatrix} A & B & 0 & 0 & \dots & B' \\ B' & A & B & 0 & \dots & 0 \\ 0 & B' & A & B & \dots & 0 \\ 0 & 0 & B' & A & \dots & 0 \\ & & & & \dots A & B \\ B & 0 & 0 & 0 & \dots B' & A \end{bmatrix} \qquad -(23)$$

where A and B are, respectively, the matrices

$$\begin{bmatrix} \alpha^P & 0 & -a \\ 0 & \alpha^P & a \\ -a & a & \alpha^N \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} -b & -b & 0 \\ b & b & 0 \\ -a & -a & 0 \end{bmatrix} \qquad -(24)$$

and where 0 represents the 3x3 null matrix.

The matrices (23) and (24) are analogous to those obtained in section 6.5 using the Huckel method.

(f) The bond order matrix also possessed, for $\delta\omega_{\mu}^{P} = \delta\omega_{\mu'}^{P}$, a structure similar to (23). For $(PN)_3$ for example, with a modification of the type c(iii) above, the bond order matrix was of the form

$$\begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} & \frac{1}{4} & \frac{1}{4} & 0 & \frac{1}{4} & -\frac{1}{4} & \frac{1}{2} \\ 0 & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{4} & -\frac{1}{4} & 0 & \frac{1}{4} & -\frac{1}{4} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & 1 & \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\ \frac{1}{4} & -\frac{1}{4} & \frac{1}{2} & \frac{1}{2} & 0 & \frac{1}{2} & \frac{1}{4} & \frac{1}{4} & 0 \\ \frac{1}{4} & -\frac{1}{4} & \frac{1}{2} & 0 & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{4} & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{2} & -\frac{1}{2} & 1 & \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{4} & \frac{1}{4} & 0 & \frac{1}{4} & -\frac{1}{4} & \frac{1}{2} & \frac{1}{2} & 0 & \frac{1}{2} \\ -\frac{1}{4} & -\frac{1}{4} & 0 & \frac{1}{4} & -\frac{1}{4} & \frac{1}{2} & 0 & \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{1}{2} & 1 \end{bmatrix} \qquad -(25)$$

Bond orders relating to atomic orbitals in different islands were apparently zero. For instance, consider the island (20) in $(PN)_3$. Hence $P_{16} = P_{26} = 0$, since atomic orbital ϕ_6 is not involved in either the first island (20) or the third and last island which involved ϕ_7, ϕ_8, ϕ_9, ϕ_1 and ϕ_2. Also $P_{36} = P_{37} = P_{38} = P_{39} = 0$ for a similar reason.

Many more such zero elements P_{ij} occur for larger values of n, as indicated by the general form (23) taken by the bond order matrix.

7.1.3 Theoretical Study of the SCF Model

The aim of the theoretical study was first of all to explain some of the observations arising out of the numerical experiments and then to use the information gathered to assist in deriving and verifying a theoretical solution for the SCF model.

7.1.3(a) Analysis of the SCF Matrix Diagonal Elements

A review of the expressions (8) and (9) was undertaken to ascertain why, in the first solutions obtained, the resultant α_μ^P and α_ν^N were always equal in value and opposite in sign.

Consider the expression

$$\alpha_{\mu}^{P} + \alpha_{\mu'}^{P} + 2\alpha_{\nu}^{N} \qquad -(26)$$

where μ,$\mu'$and ν refer to orbitals on neighbouring P and N atoms, and suppose $\delta\omega_{\mu}^{P} = \delta\omega_{\mu'}^{P}$, and $\gamma_{\mu\mu} = \gamma_{\mu'\mu'}$. Now, symmetry considerations suggest that

$$P_{\mu\mu} + P_{\mu'\mu'} + P_{\nu\nu} = 2 \qquad -(27)$$

and hence the four summations in the full expression (26) can be seen to cancel out.

It becomes possible, therefore, to write

$$\alpha_{\mu}^{P}+\alpha_{\mu'}^{P}+2\alpha_{\nu}^{N} = 2(\delta\overset{P}{\omega}+\delta\overset{N}{\omega}-\gamma)+\tfrac{1}{2}(P_{\mu\mu}+P_{\mu'\mu'})(\gamma_{\mu\mu}+\gamma_{\mu\mu'})+P_{\nu\nu}\gamma_{\nu\nu} \qquad -(27)$$

Hence

$$\alpha_{\nu}^{N} = -\frac{(\alpha_{\mu}^{P}+\alpha_{\mu'}^{P})}{2} + (\delta\omega^{P}+\delta\omega^{N}-\gamma) + \frac{(P_{\mu\mu}+P_{\mu'\mu'})}{2}\cdot\frac{(\gamma_{\mu\mu}+\gamma_{\mu\mu'})}{2}$$

$$+ \tfrac{1}{2} P_{\nu\nu}\,\gamma_{\nu\nu} \qquad -(28)$$

In the original computations, $\delta\omega^{P} = \delta\omega^{N} = 0$, and $\gamma_{\mu\mu} = \gamma_{\mu\mu'} = \gamma_{\nu\nu} = \gamma$,

$$\therefore\ \alpha_{\nu}^{N} = -\frac{(\alpha_{\mu}^{P}+\alpha_{\mu'}^{P})}{2} - \gamma + \frac{\gamma}{2}\ (P_{\mu\mu}+P_{\mu'\mu'}+P_{\nu\nu})$$

$$= -\frac{(\alpha_{\mu}^{P}+\alpha_{\mu'}^{P})}{2} \qquad -(29)$$

With ϕ_{μ} and $\phi_{\mu'}$ receiving equal treatment throughout it can be seen that, under the conditions stated,

$$\alpha_{\nu}^{N} = -\alpha_{\mu}^{P} = -\alpha_{\mu'}^{P} \qquad -(30)$$

Expression (28) also shows that, with $\delta\omega_{\mu}^{P} = \delta\omega_{\mu'}^{P} = 0$ and $\delta\omega_{\nu}^{N} = \overline{\delta\omega}_{\nu}^{N}$, so that $\alpha_{\mu}^{P} = \alpha_{\mu'}^{P} = 0$ and a uniform charge distribution is obtained, then $\alpha_\nu^N = \overline{\delta\omega}_\nu^N$.

Similarly, if $\delta\omega_\nu^N = 0$ and $\delta\omega_\mu^P = \delta\omega_{\mu'}^P = \overline{\delta\omega}_\mu^P$, then $\alpha_\mu = \alpha_{\mu'}^P = \overline{\delta\omega}_\mu^P$.

Henceforth, in the theoretical development of island solutions, it is assumed that

$$\begin{aligned} \alpha_\mu^P &= \alpha_{\mu'}^P \\ \gamma_{\mu\mu} &= \gamma \\ P_{\mu\mu} &= P_{\mu'\mu'} \\ \delta\omega_\mu^P &= \delta\omega_{\mu'}^P = 0 \end{aligned} \qquad -(31)$$

Then (28) may be written

$$\alpha_\nu^N = -\alpha_\mu^P + \delta\omega^N - \gamma + \tfrac{1}{2}P_{\mu\mu}\gamma + \tfrac{1}{2}P_{\mu\mu}\gamma_{\mu\mu'} + \tfrac{1}{2}P_{\nu\nu}\gamma_{\nu\nu} \qquad -(32)$$

With $\gamma_{\nu\nu}$ set equal to $\gamma_{\mu\mu} = \gamma$, this simplifies to

$$\alpha_\nu^N = -\alpha_\mu^P + \delta\omega^N + \tfrac{1}{2}P_{\mu\mu}\,(\gamma_{\mu\mu'} - \gamma) \qquad -(33)$$

7.1.3(b) Determination of SCF Energy Levels

A procedure similar to that used for finding the Huckel orbital energies was applied to the determinantal form derived from the SCF matrix (23).

Row and column operations were performed until the determinant was reduced to a form which displayed the n-fold degeneracy in three roots of p(x) = 0, where

$$\begin{aligned} p(x) &= (x+\alpha^P+2b)\left\{(x+\alpha^N)(x+\alpha^P+2b) - 4(b(x+\alpha^N)+a^2)\right\} \\ &= (x+\alpha^P+2b)\left\{(x+\alpha^N)(x+\alpha^P-2b)-4a^2\right\} \end{aligned} \qquad -(34)$$

Hence, one of the energies is always given by

$$\varepsilon = \alpha^P + 2b \qquad -(35)$$

and the other two come from the quadratic factor in (34), giving

$$\varepsilon = \frac{(\alpha^P + \alpha^N - 2b) \pm \sqrt{((\alpha^N - \alpha^P + 2b)^2 + 16a^2)}}{2} \qquad -(36)$$

In the special case where $\delta\omega^N = 0$ and $\gamma_{\mu\mu'} = \gamma$, as in the initial computed solutions, then $\alpha^P = -\alpha^N = \alpha$, and the energies are given by

$$\varepsilon = \alpha + 2b \qquad -(37)$$

and
$$\varepsilon = -b \pm \sqrt{((b-\alpha)^2 + 4a^2)} \qquad -(38)$$

7.1.3(c) Determination of SCF Island Orbitals

In the following discussion, the simplest system $(PN)_3$ is chosen for illustration, but the argument and the analytical procedures are equally applicable to PN ring systems of any size.

A formal change from the basis of atomic orbitals ϕ_i to one of θ_i, where

$$\theta_1 = \frac{\phi_1 - \phi_2}{\sqrt{2}}, \theta_2 = \phi_3, \theta_3 = \frac{\phi_4 + \phi_5}{\sqrt{2}}, \ldots, \theta_9 = \frac{\phi_1 + \phi_2}{\sqrt{2}} \qquad -(39)$$

can be made by a similarly transformation on the SCF matrix H, given in (23), using

$$U = \begin{bmatrix} T & 0 & S \\ S & T & 0 \\ 0 & S & T \end{bmatrix} \qquad -(40)$$

where, once more, 0 is the 3x3 null matrix, and S and T are, respectively, the matrices

$$\begin{bmatrix} 0 & 0 & \frac{1}{\sqrt{2}} \\ 0 & 0 & \frac{1}{\sqrt{2}} \\ 0 & 0 & 0 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} \frac{1}{\sqrt{2}} & 0 & 0 \\ \frac{-1}{\sqrt{2}} & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \qquad -(40)$$

Then U^{-1} HU takes on the diagonal form

$$\begin{bmatrix} W & 0 & 0 \\ 0 & W & 0 \\ 0 & 0 & W \end{bmatrix} \qquad -(41)$$

where W is given by

$$W \equiv \begin{bmatrix} \alpha^P & -a\sqrt{2} & -2b \\ -a\sqrt{2} & \alpha^N & -a\sqrt{2} \\ -2b & -a\sqrt{2} & \alpha^P \end{bmatrix} \qquad -(42)$$

Hence island orbitals can be found, with forms in the θ basis

(i) $c_1, c_2, c_3, 0, 0, 0, 0, 0, 0$

(ii) $0, 0, 0, c_1, c_2, c_3, 0, 0, 0$

and (iii) $0, 0, 0, 0, 0, 0, c_1, c_2, c_3$. (43)

Each distinct energy level gives rise to a set such as (43), and the coefficients can be found by solving the eigenvalue equations

$$W \underline{c}_i = \varepsilon_i \underline{c}_i \qquad -(44)$$

Solutions of (44) with

(a) $c_1 = -c_3, c_2 = 0$,

(b) $c_1 = c_3, c_2 = r_1 c_1$,

and (c) $c_1 = c_3, c_2 = -r_2 c_1$

can be obtained by substituting (35) and (36) in (44) giving

(a) $c_1 = \frac{1}{\sqrt{2}}$, $c_2 = 0$, $c_3 = -\frac{1}{\sqrt{2}}$ (45)

(b) $c_1 = c_3 = \frac{1}{\sqrt{2+r_1{}^2}}$, $c_2 = \frac{r_1}{\sqrt{2+r_1{}^2}}$,

$$\text{where } r_1 = \frac{(\alpha^P-\alpha^N-2b) + \sqrt{((\alpha^P-\alpha^N-2b)^2 + 16a^2)}}{2\sqrt{2}a} \qquad -(46)$$

$$\text{(c)} \quad c_1 = c_3 = \frac{1}{\sqrt{2+r_2{}^2}} \, , \quad c_2 = \frac{-r_2}{\sqrt{2+r_2{}^2}}$$

$$\text{where } -r_2 = \frac{(\alpha^P-\alpha^N-2b) - \sqrt{((\alpha^P-\alpha^N-2b)^2 + 16a^2)}}{2\sqrt{2a}} \qquad -(47)$$

These are equivalent to the forms (22), (20) and (21) in the original basis. When $\alpha^P = \alpha = -\alpha^N$, the expressions (46) and (47) reduce to

$$r_1, -r_2 = \frac{\alpha-b \pm \sqrt{(\alpha-b)^2 + 4a^2}}{\sqrt{2}a} \qquad -(48)$$

7.1.3(d) Bond Order Matrix Analysis

This matrix is clearly important in maintaining the steady form of the SCF matrix. Its properties can be investigated more easily by considering its generation from the occupied orbitals in the θ basis. For $(PN)_3$ the occupied island orbitals may be written (dropping the subscript on r_1)

$$\begin{aligned}
&\text{(i)}\ \underline{u}_1 \equiv \frac{1}{\sqrt{2+r^2}}, \frac{r}{\sqrt{2+r^2}}, \frac{1}{\sqrt{2+r^2}}, \ 0 \ , \ 0 \ , \ 0 \quad 0 \ , \ 0 \ , \ 0 \\
&\text{(ii)}\ \underline{u}_2 \equiv \ 0 \ , \ 0 \ , \ 0 \ , \frac{1}{\sqrt{2+r^2}}, \frac{r}{\sqrt{2+r^2}}, \frac{1}{\sqrt{2+r^2}} \ 0 \ , \ 0 \ , \ 0 \\
&\text{(iii)}\ \underline{u}_3 \equiv \ 0 \ , \ 0 \ , \ 0 \ , \ 0 \ , \ 0 \ , \ 0 \ \frac{1}{\sqrt{2+r^2}}, \frac{r}{\sqrt{2+r^2}}, \frac{1}{\sqrt{2+r^2}}
\end{aligned} \qquad -(49)$$

A delocalised MO $\underline{w}_i$ can be constructed as a linear combination of $\underline{u}_1, \underline{u}_2$ and $\underline{u}_3$.

$$\underline{w}_i = a_i \, \underline{u}_1 + b_i \, \underline{u}_2 + c_i \, \underline{u}_3 \qquad -(50)$$

where a_i, b_i, c_i are normalised coefficients, and $\underline{w}_i \cdot \underline{w}_j = 0$ if $i \neq j$

Thus if $\underline{w}_1$, $\underline{w}_2$, $\underline{w}_3$ are any three such MO's, they can be written

$$\begin{bmatrix} \underline{w}_1 \\ \underline{w}_2 \\ \underline{w}_3 \end{bmatrix} = \begin{bmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{bmatrix} \cdot \begin{bmatrix} \underline{u}_1 \\ \underline{u}_2 \\ \underline{u}_3 \end{bmatrix} \qquad -(51)$$

where the 3x3 matrix in (51) possesses the property of orthogonality, because, by definition, its transpose is orthogonal.

Consider now the bond order matrix element P_{16} (in terms the original ϕ basis)

$$\text{Now } \phi_1 = \frac{\theta_1 + \theta_9}{\sqrt{2}} \text{ and } \phi_6 = \theta_5 \text{ , } \qquad \text{from (39)}$$

$$\text{Therefore } P_{16} = 2 \sum_{k=1}^{3} w_{k1} \cdot w_{k6}$$

$$= 2 \sum_{k=1}^{3} \frac{a_k + c_k}{\sqrt{2}\,\sqrt{2+r^2}} \cdot \frac{b_k r}{\sqrt{2+r^2}}$$

$$= 0 \text{ ,} \qquad -(52)$$

by virtue of the orthogonality of the matrix in (51).

A similar result follows for any matrix element $P_{\mu\nu}$, linking atomic orbitals in different islands.

Hence zero-valued elements appear in the general bond order matrix as indicated by (23).

The bond-order sub-matrices A and B in the general expression (23) may be found, in terms of r only, by calculations of the type (52)

$$\text{e.g.} \quad P_{11} = 2 \sum_{k=1}^{3} w_{k1} \cdot w_{k1}$$

$$= 2 \sum_{k=1}^{3} \frac{a_k + c_k}{\sqrt{2}\,\sqrt{2+r^2}} \cdot \frac{a_k + c_k}{\sqrt{2}\,\sqrt{2+r^2}}$$

$$= 2 \times \frac{2}{2(2+r^2)} = \frac{2}{2+r^2}$$

-(53)

$$\text{and} \quad P_{23} = 2 \sum_{k=1}^{3} \frac{c_k - a_k}{\sqrt{2}\,\sqrt{2+r^2}} \cdot \frac{a_k r}{\sqrt{2+r^2}} = \frac{-\sqrt{2}r}{2+r^2} \qquad -(54)$$

so that

$$A = \begin{bmatrix} \frac{2}{2+r^2} & 0 & \frac{\sqrt{2}r}{2+r^2} \\ 0 & \frac{2}{2+r^2} & \frac{-\sqrt{2}r}{2+r^2} \\ \frac{\sqrt{2}r}{2+r^2} & \frac{-\sqrt{2}r}{2+r^2} & \frac{2r^2}{2+r^2} \end{bmatrix}, \quad B = \begin{bmatrix} \frac{1}{2+r^2} & \frac{1}{2+r^2} & 0 \\ \frac{-1}{2+r^2} & \frac{-1}{2+r^2} & 0 \\ \frac{\sqrt{2}r}{2+r^2} & \frac{\sqrt{2}r}{2+r^2} & 0 \end{bmatrix} \qquad -(55)$$

Thus, when $\alpha^P - \alpha^N = 2b$, it may be seen from (46) that $r = \sqrt{2}$, giving for $(PN)_3$ the uniform bond order matrix (25).

The condition identified experimentally in 7.1.2(c) (iii) for obtaining a solution of the type (10) may, therefore be stated as

$$\overline{\delta\omega}_\mu^{\,P} = -\overline{\delta\omega}_\nu^{\,N} = 2b \, . \qquad -(56)$$

7.1.3(e) Structure of the SCF matrix

A valid start to the SCF iterative procedure is given by the Huckel-type island orbitals, obtained by putting $r = \sqrt{2}$ in the expressions for $\underline{u}_1$, $\underline{u}_2$ and $\underline{u}_3$ given in 7.1.3(d). After transforming these back to the original ϕ basis, a bond order matrix with a form similar to (25) is first generated, and the initial SCF matrix, calculated from (3), (8) and (9), then has the structure (23).

It has been seen that, when diagonalised, such an SCF matrix leads to SCF MO's which are linear combinations of the island MO's, e.g. (20), (21), (22), and these have now been shown always to give rise to a particular form of bond order matrix (23, (25), where elements involving atomic orbitals on different islands are zero.

Hence the structure (23) of the initial SCF matrix is maintained throughout the iterations, despite the inclusion of 'inter-island' off-diagonal terms as indicated by (3), and the SCF process converges under the stated conditions to a solution which may be expressed in terms of SCF island orbitals.

7.1.4 A Program for Finding SCF Island Orbitals and Energies

Writing
$$s = \alpha^P - \alpha^N - 2b \qquad -(57)$$

the expressions (46) and (47) for r_1, r_2 may be conveniently written

$$r_1, -r_2 = \frac{s \pm \surd(s^2+16a^2)}{2\sqrt{2}a} \qquad -(58)$$

from which the SCF island orbitals may be readily derived.

The energies are then given by

$$\varepsilon = \alpha^N - \sqrt{2}ar_2 \qquad \text{(lowest)}, \qquad -(59)$$

$$\varepsilon = \alpha^P + 2b \qquad , \qquad -(60)$$

and
$$\varepsilon = \alpha^N + \sqrt{2}ar_1 \qquad \text{(highest)}. \qquad -(61)$$

Hence the complete solution is given in terms of r_1 and r_2, and a and b, which themselves are functions of r_1 and r_2.

In fact the expression (58) defines a first order iterative process, analagous to the SCF process, for finding r_1 and r_2. However, unlike the SCF procedure, there are no matrix manipulations involved until the iterative part is complete, and r_1 and r_2 have been obtained to the desired accuracy. Then all that is required is the final computation of the set of island orbital coefficients in the forms (20), (21) and (22) etc.

The variables a and b are given by

$$a = \beta_a + \gamma_a P_a/2 \qquad -(62)$$

and $$b = \gamma_b P_b/2 \qquad 1(63)$$

where the sub-scripts a and b refer to nearest neighbours and next nearest neighbours respectively.

Then $$P_a = \sqrt{2}r/(2+r^2) \qquad -(64)$$

and $$P_b = 1/(2+r^2) \qquad -(65)$$

The diagonal elements of the SCF matrix may now be expressed

$$\alpha_\mu^P = \delta\omega_\mu^P - \tfrac{1}{2}\gamma + \left\{\gamma_{\mu\mu} + \gamma_{\mu\mu'} + (2-r^2)\left(\sum_{\substack{P\\ \lambda\neq\mu}}\gamma_{\mu\lambda} - \sum_{\substack{N\\ \sigma\neq\mu}}\gamma_{\mu\sigma}\right)\right\}/(2+r^2) \qquad -(66)$$

and $$\alpha_\nu^N = \delta\omega_\nu^N - \alpha_\mu^P + (\gamma_{\mu\mu'} - \gamma_{\mu\mu})/(2+r^2) \qquad -(67)$$

Based on these expressions, a FORTRAN subroutine AORBS was written in order to calculate SCF island orbitals for $(PN)_n$ cyclic systems.

Input requirements of AORBS are

N - no. of atoms in the system

UN - parameter $\delta\omega_\nu^N$

BETA - core integral β_a

HFGAM $\equiv \gamma$

GG - two-component vector $\gamma_{\mu\mu}$ and $\gamma_{\mu\mu'}$

GGG - vector of N-1 repulsion integrals $\gamma_a, \gamma_b, \gamma_c, \ldots, \gamma_b, \gamma_a$

NIT - number of iterations

Output consists of

E - vector of three energy levels

R - ratio r_1 and r_2

T - $\frac{3N}{2} \times \frac{3N}{2}$ array of island orbitals

The subroutine uses (66) with $\delta\omega_\mu^P = 0$ and $\gamma_{\mu\mu} = \gamma_{\nu\nu}$, regarding $\delta\omega_\nu^N$ as a parameter which can incorporate changes to $\delta\omega_\mu^P$ or to $\gamma_{\nu\nu}$. A Huckel island orbital start to the iterative procedure is built into the subroutine.

AORBS made it possible to generate SCF solutions in a fraction of the time required by the conventional SCF procedure, but with similar accuracy, and using no more core space for large problems than was needed for the smallest system. This proved extremely valuable as attention was turned to CI solutions for these systems.

The text of AORBS is given overleaf.

```
      SUBROUTINE AORBS(N,UN,BETA,HEGAM,NIT,GGG,GG,T,FDIAG,F,R)
      DIMENSION T(30,30),FDIAG(30)
      DIMENSION F(3),R(2),C(15),GGG(19),GG(2)
      SR=SQRT(2.0)
      R(1)=SR
      R(2)=SR
      GGS=GG(1)+GG(2)
      GGD=GG(1)-GG(2)
      GP=0.0
      GN=0.0
      N1=NAT-1
      DO 21 J=1,N1,2
   21 GN=GN+GGG(J)
      N2=NAT-2
      DO 2 J=2,N2,2
    2 GP=GP+GGG(J)
      GD=GP-GN
      DO 10 I=1,NIT
      RR=R(1)*R(1)+2
      RA=R(1)/RR/SR
      RB=0.5/RR
      A=-BETA+GGG(1)*RA
      B=GGG(2)*RB
      A1=-HEGAM+(GGS+(4-RR)*GD)/RR
      A3=UN-A1-GGD/RR
      W=A1-A3-2*B
      X=W+2*A3
      Z=SQRT(W*W+16*A*A)
      F(1)=(X-Z)/2
      F(2)=2*B+A1
      F(3)=(X+Z)/2
      IF(NIT-I)10,10,3
    3 D=2*SR*A
      R(1)=(W+Z)/D
      R(2)=(-W+Z)/D
   10 CONTINUE
      R1=SQRT(2+R(1)*R(1))
      R2=SQRT(2+R(2)*R(2))
```

```
      C(1)=1/SR/R1
      C(2)=-C(1)
      C(3)=R(1)/R1
      C(4)=C(1)
      C(5)=C(1)
      C(6)=0.5
      C(7)=-0.5
      C(8)=0.0
      C(9)=-0.5
      C(10)=-0.5
      C(11)=1/SR/R2
      C(12)=-C(11)
      C(13)=-R(2)/R2
      C(14)=C(11)
      C(15)=C(11)
      DO 1 I=1,N
      DO 1 J=1,N
    1 T(I,J)=0.0
      KI=N/3
      DO 111 K=KI,N,KI
      KK=K/KI
      DO 111 J=1,KI
      JJ=J+K-KI
      FDIAG(JJ)=F(KK)
      DO 111 I=1,5
      II=I+3*(JJ-1)
      III=I+5*(KK-1)
      IF(II-N)72,72,73
   73 II=II-N*(II/N)
      IF(II)72,40,72
   40 II=N
   72 T(II,JJ)=C(III)
  111 CONTINUE
      RETURN
      END
```

7.2 The CI Method

The numerical and theoretical results established in the previous section enabled progress to be made with a study of the CI problem based on single orbital replacement configurations derived from SCF island orbital ground state solutions.

The study is of interest for the light it sheds on the question of the influence of the island orbital solution on the UV spectrum. Dewar, {1}, suggests that this remains substantially constant as the size of the $(PN)_n$ ring increases with n. However, numerical evidence arising out of extended CI calculations using SCF island orbitals derived from AORBS, and a subsequent theoretical solution of the complete SCF-CI island model would appear to suggest that Dewar's assertion is incorrect.

7.2.1 The CI Matrix

The CI matrix diagonal elements for single replacements based on SCF orbitals may be written

$$\langle i\to k'|h_\pi|i\to k'\rangle = \Delta E_{ik'} \pm (ik'|k'i) \qquad -(66)$$

with

$$\Delta E_{ik'} = \varepsilon_{k'}-\varepsilon_i-\{(ik'|ik')-(ik'|k'i)\} \qquad -(67)$$

where + and - signs refer to singlet and triplet configurations respectively, and where E_o, the SCF ground state energy has been adopted as the zero of energy by effectively subtracting E_o from all diagonal terms. The off-diagonal elements are given by

$$\langle i\to k'|h_\pi|j\to \ell'\rangle = -\{(i\ell'|jk')-(i\ell'|k'j)\} \pm (i\ell'|k'j) \qquad -(68)$$

ε_i are SCF orbital energies, and $(ij|k\ell)$ are electron-repulsion integrals expressed in terms of SCF MO's ψ_i, ψ_j,... etc. In the overlap approximation, these integrals may be expressed in terms of the coefficients of the basic atomic orbitals and the related electron repulsion integrals $\gamma_{\mu\nu}$

$$\Sigma(ij|k\ell) = \sum_{\mu} c_{\mu i}c_{\mu k} \sum_{\nu} c_{\nu j}c_{\nu\ell}\, \gamma_{\mu\nu} \qquad -(69)$$

The CI matrix will now be constructed in the θ basis defined in section 7.1, so that $\psi_i, \psi_j, \ldots$etc above refer to SCF island orbitals, and $\gamma_{\mu\nu}$ now refers to θ_μ and θ_ν.

Consider only $(PN)_3$ in the first instance, and let the SCF island orbitals ψ_j and their associated energy levels ε_j be numbered as follows

j	ψ_j								
1	$\frac{1}{\sqrt{2+r_1^2}}$	$\frac{r_1}{\sqrt{2+r_1^2}}$	$\frac{1}{\sqrt{2+r_1^2}}$	0	0	0	0	0	0
2	0	0	0	$\frac{1}{\sqrt{2+r_1^2}}$	$\frac{r_1}{\sqrt{2+r_1^2}}$	$\frac{1}{\sqrt{2+r_1^2}}$	0	0.	0
3	0	0	0	0	0	0	$\frac{1}{\sqrt{2+r_1^2}}$	$\frac{r_1}{\sqrt{2+r_1^2}}$	$\frac{1}{\sqrt{2+r_1^2}}$
4	$\frac{1}{\sqrt{2}}$	0	$\frac{-1}{\sqrt{2}}$	0	0	0	0	0	0
5	0	0	0	$\frac{1}{\sqrt{2}}$	0	$\frac{-1}{\sqrt{2}}$	0	0	0
6	0	0	0	0	0	0	$\frac{1}{\sqrt{2}}$	0	$\frac{-1}{\sqrt{2}}$
7	$\frac{1}{\sqrt{2+r_2^2}}$	$\frac{-r_2}{\sqrt{2+r_2^2}}$	$\frac{1}{\sqrt{2+r_2^2}}$	0	0	0	0	0	0
8	0	0	0	$\frac{1}{\sqrt{2+r_2^2}}$	$\frac{-r_2}{\sqrt{2+r_2^2}}$	$\frac{1}{\sqrt{2+r_2^2}}$	0	0	0
9	0	0	0	0	0	0	$\frac{1}{\sqrt{2+r_2^2}}$	$\frac{-r_2}{\sqrt{2+r_2^2}}$	$\frac{1}{\sqrt{2+r_2^2}}$

-(70)

Thus levels 1,2 and 3 are occupied and levels 6 to 9 are unoccupied. The CI matrix constructed from the nine possible single replacements amongst SCF island MO's describing the six lowest levels then has the form

$$\begin{array}{c|ccccccccc}
 & 3\text{-}4 & 3\text{-}5 & 3\text{-}6 & 2\text{-}4 & 2\text{-}5 & 2\text{-}6 & 1\text{-}4 & 1\text{-}5 & 1\text{-}6 \\
\hline
3\text{-}4 & c & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
3\text{-}5 & 0 & c & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
3\text{-}6 & 0 & 0 & \bar{a} & 0 & a_1 & 0 & a_1 & 0 & 0 \\
2\text{-}4 & 0 & 0 & 0 & c & 0 & 0 & 0 & 0 & 0 \\
2\text{-}5 & 0 & 0 & a_1 & 0 & \bar{a} & 0 & a_1 & 0 & 0 \\
2\text{-}6 & 0 & 0 & 0 & 0 & 0 & c & 0 & 0 & 0 \\
1\text{-}4 & 0 & 0 & a_1 & 0 & a_1 & 0 & \bar{a} & 0 & 0 \\
1\text{-}5 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & c & 0 \\
1\text{-}6 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & c
\end{array} \qquad -(71)$$

The diagonal element $c = \langle 3\to 4' \mid h_\pi \mid 3\to 4' \rangle$ for example is given by

$$\varepsilon_4-\varepsilon_3-\sum_\mu c_{\mu 3}^2 \sum_\nu c_{\nu 4}^2\, \gamma_{\mu\nu}+2\sum_\mu c_{\mu 3}c_{\mu 4} \sum_\nu c_{\nu 3}c_{\nu 4}\, \gamma_{\mu\nu} \qquad -(72)$$

The second of the two summation terms is zero due to the independence of the island orbitals, whereas

$$\sum_\mu c_{\mu 3}^2 \sum_\nu c_{\nu 4}^2 \gamma_{\mu\nu} = \frac{1}{2+r_1^2}\left(\frac{\gamma_{71}}{2}+\frac{\gamma_{73}}{2}\right)+\frac{r_1^2}{2+r_1^2}\left(\frac{\gamma_{81}}{2}+\frac{\gamma_{83}}{2}\right)+\frac{1}{2+r_1^2}\left(\frac{\gamma_{91}}{2}+\frac{\gamma_{93}}{2}\right) \qquad -(73)$$

The diagonal elements c relate to excitations between islands, and may be distinguished from those elements relating to excitations within islands. For example $\bar{a} = \langle 3\to 6' | h_\pi | 3\to 6' \rangle$ is given by

$$\varepsilon_6-\varepsilon_3-\sum_\mu c_{\mu 3}^2 \sum_\nu c_{\nu 6}^2 \gamma_{\mu\nu}+2\sum_\mu c_{\mu 3}c_{\mu 6}\sum_\nu c_{\nu 3}c_{\nu 6}\gamma_{\mu\nu} \qquad -(74)$$

This time the second integral is not zero, and is given by

$$\sum_{\mu} c_{\mu 3} c_{\mu 6} \sum_{\nu} c_{\nu 3} c_{\nu 6} \gamma_{\mu\nu} = \frac{1}{2(2+r_1{}^2)}(\gamma_{77}-\gamma_{79}) - \frac{1}{2(2+r_1{}^2)}(\gamma_{97}-\gamma_{99}) \qquad -(75)$$

Most of the off-diagonal elements are zero due to the independence of island orbitals. The non-zero elements indicate which single replacement functions combine when CI methods are introduced. In fact, only configurations relating to excitations within individual islands interact in this manner, and the appropriate CI matrix elements may be derived as indicated above for diagonal elements.

7.2.2 The CI Solution

The CI matrix (71) can be factorised, and the eigenvalues E_j obtained from the six single factors corresponding to the diagonal elements c and the cubic associated with the 3x3 submatrix

$$\begin{bmatrix} \bar{a} & a_1 & a_1 \\ a_1 & \bar{a} & a_1 \\ a_1 & a_1 & \bar{a} \end{bmatrix} \qquad -(76)$$

Therefore, the nine state energies, relative to the SCF ground state, are

$$E_1 = \bar{a} + 2a_1 \qquad (77)$$

$$E_2 = E_3 = \bar{a}-a_1 \qquad (78)$$

$$E_j = c, \; j=4,\ldots,9 \qquad -(79)$$

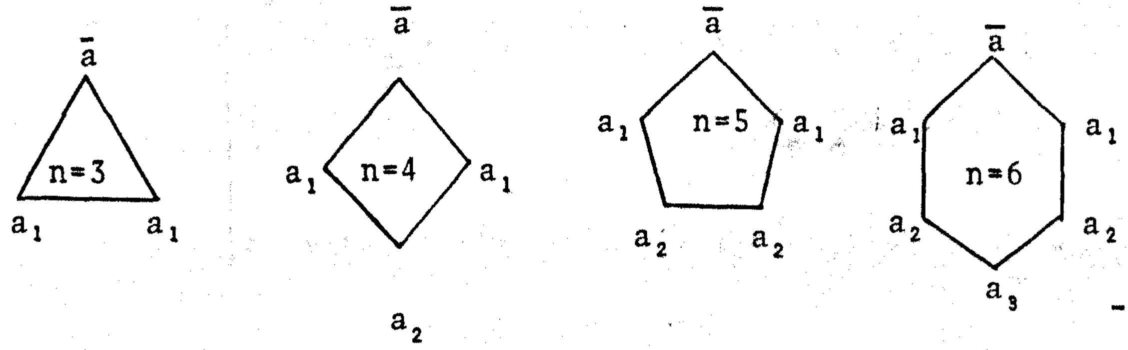
The state wave functions Φ corresponding to E_1, E_2 and E_3 may then be obtained in the forms

$$\Phi_1 = \frac{1}{\sqrt{3}}\left\{\Psi(3\to6')+\Psi(2\to5')+\Psi(1\to4')\right\} \qquad -(80)$$

$$\Phi_2 = \frac{1}{\sqrt{2}}\left\{\Psi(3\to6')-\Psi(2\to5')\right\} \qquad -(81)$$

$$\Phi_3 = \frac{1}{\sqrt{2}}\left\{\Psi(2\to5')-\Psi(1\to4')\right\} \qquad -(82)$$

The sub-matrix (76) for n = 3 islands can be written down for larger systems by recognising the following geometrical relationship between matrix elements which reflects the distances between islands.



-(83)

The general determinantal equation for the E_j corresponding to (77) and (78) may then be written

$$C_n \; (n \text{ even}) = \begin{vmatrix} a_o & a_1 & \cdots & a_{n/2-1}, & a_{n/2}, & a_{n/2-1} & \cdots\cdots & & a_1 \\ a_1 & a_o & \cdots & a_{n/2-2}, & a_{n/2-1}, & a_{n/2} & \cdots\cdots & & a_2 \\ \vdots & & & & & & & & \vdots \\ & & & & & & & a_o & a_1 \\ a_1 & a_2 & & \cdots\cdots & \cdots\cdots & \cdots\cdots & & a_1 & a_o \end{vmatrix} = 0 \qquad -(84)$$

or

$$C_n \; (n \text{ odd}) = \begin{vmatrix} a_o & a_1 & \cdots & a_{(n-1)/2} & a_{(n-1)/2} & \cdots\cdots & & a_1 \\ a_1 & a_o & & a_{(n-3)/2} & a_{(n-1)/2} & \cdots\cdots & & a_2 \\ \vdots & & & & & & & \vdots \\ & & & & & & a_o & a_1 \\ a_1 & a_2 & & \cdots\cdots & \cdots\cdots & & a_1 & a_o \end{vmatrix} = 0 \qquad -(85)$$

where $a_o = \bar{a} - E$.

The determinants in (84) and (85) may be factorised by the following procedure.

Construct the modified determinant C_n' by adding τ^r times column r to column 1, where $\tau^r = 1$, i.e. τ_r $(r = 0,\dots,n-1)$ are the n roots of unity.

Thus
$$C_n' = \begin{vmatrix} a_o + \tau a_1 + \tau^2 a_2 + \dots + a_1\tau^{n-1}, & a_1 & \dots\dots & a_1 \\ a_1 + \tau a_o + \tau^2 a_1 + \dots + a_2\tau^{n-1}, & a_o & \dots\dots & a_2 \\ \vdots & & & \vdots \\ a_1 + \tau a_2 + \tau^2 a_3 + \dots\dots + a_o\tau^{n-1}, & a_2 & \dots\dots & a_o \end{vmatrix} \quad -(86)$$

Because $\tau^n = 1$, each term in the first column of C_n' possesses a factor $(a_o + \tau a_1 + \tau^2 a_2 + \dots + a_1\tau^{n-1})$ which is multiplied by τ^{i-1} in row i. However, since there are n values of τ_r, there must be n such factors, and C_n' factorises into their product, multiplied by a scalar

$$T = \begin{vmatrix} 1 & a_1 & \dots & a_1 \\ \tau & a_o & \dots & a_2 \\ \tau^2 & a_1 & \dots & a_3 \\ \tau^{n-1} & a_2 & \dots & a_o \end{vmatrix} \quad -(87)$$

Hence $C_n = 0$ may be re-expressed in terms of a product of factors

$$C_n = \prod_{r=1}^{r=n} \left\{ a_o\tau_o + \sum_{s=1}^{n/2-1} a_s(\tau_r^s + \tau_r^{n-s}) + a_{n/2}\tau_r^{n/2} \right\} = 0 \quad -(88)$$

and

$$C_n = \prod_{r=1}^{r=n} \left\{ a_o\tau_o + \sum_{s=1}^{(n-1)/2} a_s(\tau_r^s + \tau_r^{n-s}) \right\} = 0 \quad -(89)$$

for n even and n odd respectively.

The results for n = 3,4,5 and 6 are summarised below

n	Form of factor	$\tau_r(r=0,\ldots,n-1)$
3	$a_0+a_1(\tau_r+\tau_r^{2})$	$1,w,w^2$ $(w^3=1)$
4	$a_0+a_1(\tau_r+\tau_r^{3})+a_2\tau_r^{2}$	$1,i,-1,-i$
5	$a_0+a_1(\tau_r+\tau_r^{4})+a_2(\tau_r^2+\tau_r^{3})$	$1,v,v^2,\bar{v}^2,\bar{v}$ $(v^5=1)$
6	$a_0+a_1(\tau_r+\tau_r^{5})+a_2(\tau_r^3+\tau_r^{4})+a_3\tau_r^3$	$1,w^2,w,-1,-w^2,-w$

The factors may be obtained in their real form by making use of the result $\tau_r^{\ s}=\tau_1^{rs}$. These are given below for n = 3,4,5 and 6.

n	C_n
3	$(a_0+2a_1)(a_0-a_1)^2$
4	$(a_0+2a_1+a_2)(a_0-a_2)^2(a_0-2a_1+a_2)$
5	$(a_0+2a_1+2a_2)(a_0+\frac{\sqrt{5-1}}{2}a_1-\frac{\sqrt{5+1}}{2}a_2)^2(a_0-\frac{\sqrt{5+1}}{2}a_1+\frac{\sqrt{5+1}}{2}a_2)^2$
6	$(a_0+2a_1+2a_2+a_3)(a_0+a_1-a_2-a_3)^2(a_0-a_1-a_2+a_3)^2(a_0-2a_1+2a_2-a_3)$

(It is interesting to note that the modified Huckel determinants, P_n, of the previous chapter, are simplified forms of the determinants C_n as given in (84) and (85). They may be obtained by putting $a_0 = p$ and $a_1 = \gamma$, with all other $a_s = 0$. Consequently the Huckel determinants may be solved by the technique used for C_n, or, conversely, P_n may be deduced from the factors of C_n given immediately above).

7.2.3 Calculation of UV Spectra

The lowest state energy is always associated with the first (τ_o) factor of C_n, and the corresponding state wave function always possesses a form analagous to that given for $(PN)_3$ in (80). Then, because of symmetry, component transition moments at this level are zero.

This is also the case for all E_j except the second lowest (doubly degenerate) τ_i level which always indicates the only non-zero intensity band.

Hence the energy of excitation may be written

$$\Delta E = \bar{a} + \sum_{s=1}^{n/2-1} a_s \left(2\cos\frac{2\pi s}{n}\right) - a_{n/2} \qquad \text{(n even)} \quad -(90)$$

$$\text{or} \quad \Delta E = \bar{a} + \sum_{s=1}^{(n-1)/2} a_s \left(2\cos\frac{2\pi s}{n}\right) \qquad \text{(n odd)} \quad -(91)$$

The diagonal elements, $\bar{a}$, and the off-diagonal elements a_s may all be expressed in terms of SCF parameters.

Considering $\bar{a}$ first, and using the expressions (37) and (38) for SCF orbital energies, and expression (48) for r_1, r_2, the general expression for $\bar{a}$, namely

$$\varepsilon_{k'} - \varepsilon_i - \sum_\mu c_{\mu i}{}^2 \sum_\nu c_{\nu k'}^2 \gamma_{\mu\nu} + 2\sum_\mu c_{\mu i} c_{\mu k'} \sum_\nu c_{\nu i} c_{\nu k'} \gamma_{\mu\nu} \qquad -(92)$$

simplifies, to give

$$\bar{a} = \sqrt{2}\,\beta r_1 + \frac{(\gamma_a r_1^2 + 2\gamma_b)}{(2+r_1{}^2)} - \frac{(\gamma + \gamma_b + \gamma_a r_1^2)}{(2+r_1{}^2)} + 2\,\frac{(\gamma - \gamma_b)}{(2+r_1{}^2)}$$

$$= \sqrt{2}\,\beta r_1 + \frac{(\gamma - \gamma_b)}{(2+r_1{}^2)} \qquad -(93)$$

The off-diagonal elements a_s can all be written as

$$a_s = \langle 1 \rightarrow (n+1)' | h_\pi | (1+s) \rightarrow (n+1+s)' \rangle\ , \quad s = 1,2,\ldots \qquad -(94)$$

and this reduces to

$$a_s = (\gamma_{1,3s+1}-\gamma_{1,3s+3})-(\gamma_{3,3s+1}-\gamma_{3,3s+3})\ /(2+r_1{}^2) \qquad -(95)$$

Hence by substituting (93) and (95) into (90) and (91), ΔE may be found in terms of $\gamma_{\mu\nu}$, r_1 and the constant β.

For example with n = 3 islands,

$$\Delta E = \sqrt{2}\,\beta_a r_1 + \frac{(\gamma-\gamma_b)}{(2+r_1{}^2)} + 2(-\tfrac{1}{2})\,\frac{(\gamma_{14}-\gamma_{16}-\gamma_{11}+\gamma_{13})}{(2+r_1{}^2)} \qquad -(96)$$

For n = 4 islands,

$$\Delta E = \sqrt{2}\;\beta_a r_1 + \frac{(\gamma-\gamma_b)}{(2+r_1{}^2)} + 2\left\{a_1 \cos\frac{\pi}{2}\right\} - a_2$$

$$= \sqrt{2}\,\beta_a r_1 + \frac{(\gamma-\gamma_b)}{(2+r_1{}^2)} - \frac{(\gamma_{17}-\gamma_{19}-\gamma_{14}+\gamma_{16})}{(2+r_1{}^2)} \qquad -(97)$$

and so on.

In figure 7.2, ΔE is plotted against the number of atoms in the $(PN)_n$ system, and may be compared with the plot for C-C systems of similar size. Comparative oscillator strengths have also been computed and are plotted in figure 7.3 . To make comparison easier, the parameters chosen for both types of system have been made identical, so that $\gamma_{\mu\mu} = \gamma_{\mu\mu'} = \gamma_{\nu\nu} = \gamma = \gamma_{cc}$, $\delta\omega^P_\mu = \delta\omega^N_\nu = 0$, and $\beta_a = \beta =$ constant. A uniform bond length has also been taken throughout.

Hence no attempt has been made to choose parameters in order to obtain agreement with experiment. In any case, other factors, Energies of Excitation (ΔE) against no. of atoms (n)

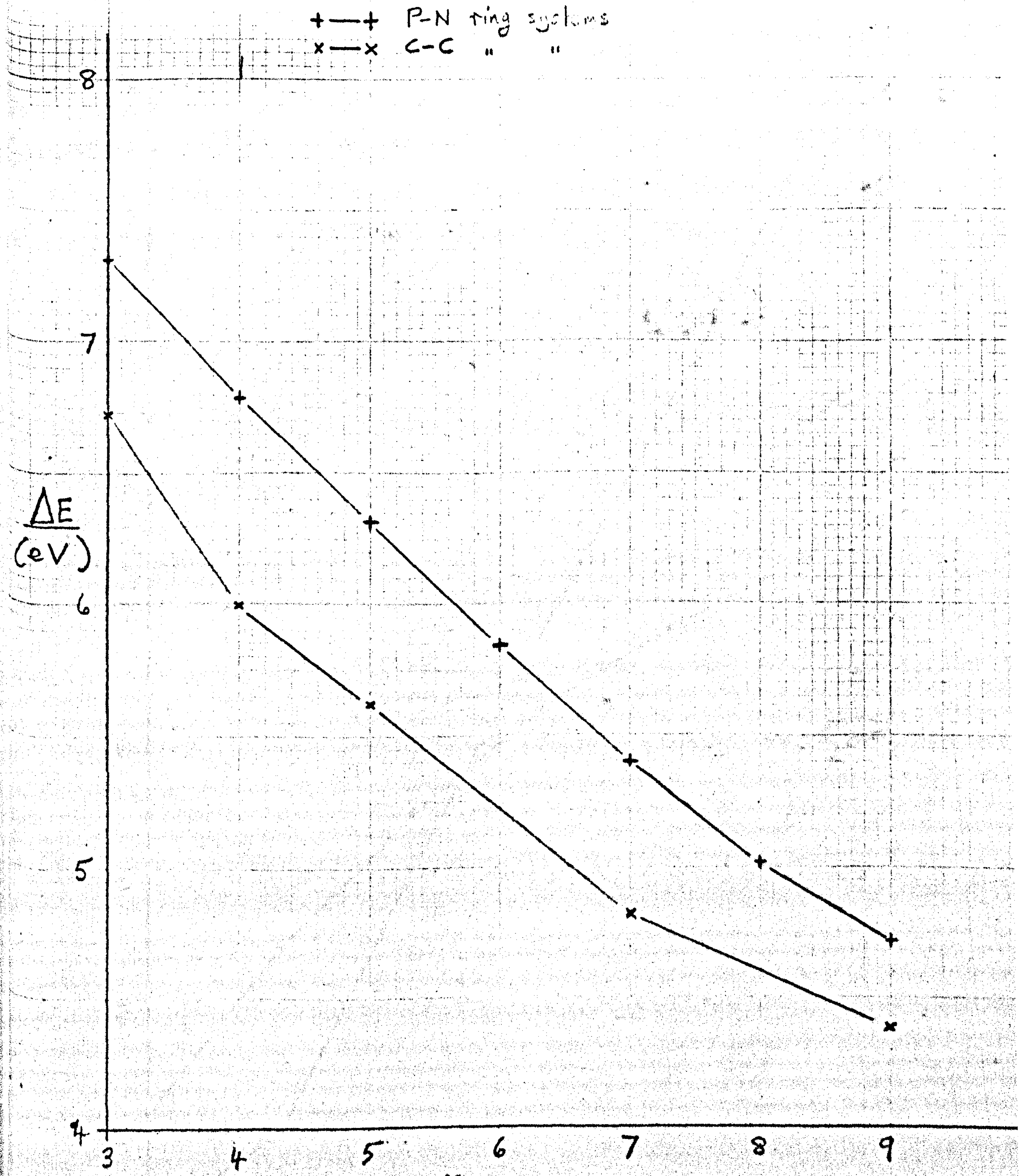


Fig. 7.2

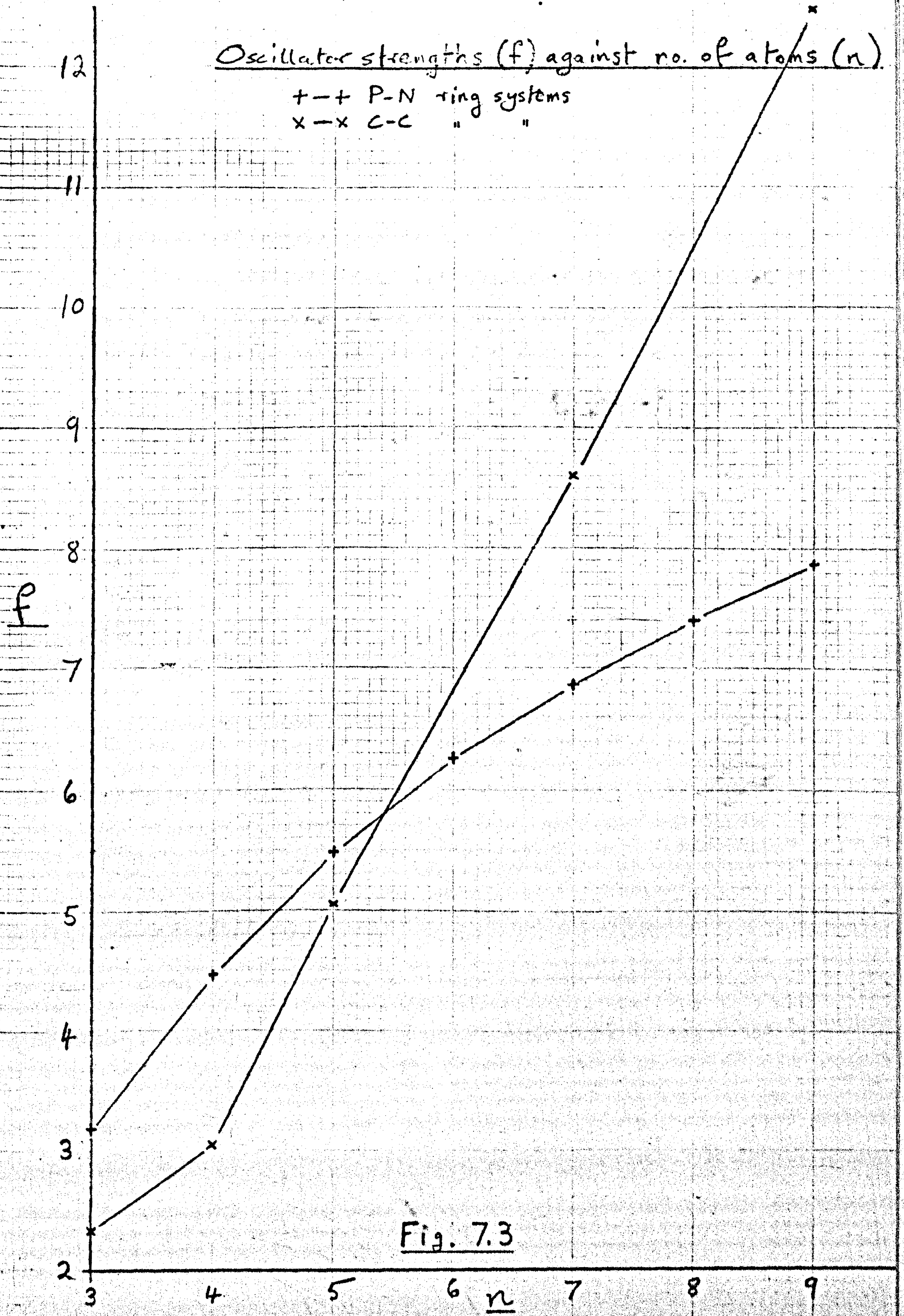

Oscillator strengths (f) against no. of atoms (n)
+—+ P-N ring systems
x—x C-C " "
f
12
11
10
9
8
7
6
5
4
3
2
3
4
5
6
7
8
9
n

Fig. 7.3

such as buckling, affect the real physical situation for both species, thereby making overall agreement with experiment difficult to obtain. Instead, the aim is to demonstrate properties of the SCF $(PN)_n$ island model in comparison with the SCF model for corresponding C-C systems.

The excitation energy plots indicate that, with equivalent parameters chosen for each, the variation with ring size is roughly parallel between PN and C-C systems. This is in contrast with the suggestion by Dewar that the energy of excitation should be largely constant with increasing n for $(PN)_n$ island systems.

7.3 Reference

{1} Dewar, M J S, Lucken, E A C and Whitehead, M A: J. Chem. Soc., p2423 (1960).

PLOTTER/DISPLAY PACKAGE

INTRODUCTION

General

The package consists of routines enabling Fortran programmers to use the digital plotter or graphical display unit more easily than is possible with the basic ICL software, and also more consistently, i.e. in the same manner for either device. Indeed there is only one version of most of the routines in the package, and the device activated depends on which low-level routines are included at run-time. (See Method of Use below). Although this means that the package cannot be used to drive both devices from one program, there is a routine for plotting the current display.

The first two sections of the package contain basic routines unique to or different for each device, and the third section contains all the general purpose routines common to both devices. Subsequent sections will contain special purpose routines and possibly basic routines for other devices - currently a group of routines for drawing graphs is available.

Although the package is based on ICL software,

routines mentioned in the Technical Manual, Sections 2.3.5 (plotter) and 2.16.3 (display) must not be used in the same program as this package.

These routines are ORIGIN, WAY, MOVE, DRAW and CENCH for the plotter, and RESET, NEWBUF, ACTION, etc. for the display. (For the benefit of already written programs, the ICL routines will continue to be available).

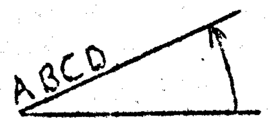
All routines in the package accessible to users have names whose first letter is G, and there are also some internal routines whose names begin with Z (except NZGTCH). Thus, users are advised to avoid using names beginning with G or Z.

Definitions

In the following paragraphs and in routine specifications, the following terms may be used:

Sheet: This is a length of plotter paper, or the display screen, and represents the boundary outside which the pen or beam is not to go. However, a main feature of the package is the suppression of all attempts to write outside the sheet, so that in some cases it can be regarded as a window for viewing parts of a larger picture.

For the plotter, the X-axis may be along or across the page, but for the display it is always horizontal.

Character angle:	Characters may be plotted at any angle. A string of characters at an oblique angle will lie on an inclined line, e.g.  The angle is measured anticlockwise from the X-axis. On the display all characters are upright and attempts to change the character angle will be ignored.
Character size:	This is the distance between the centre of successive characters plotted or displayed in a string, i.e. it includes the gap between characters. It is expressed in current units. A vertical distance 1.5 times the width will ensure no overlapping between lines.
Current units:	The units in which co-ordinates are expressed, e.g. inches or centimetres. The current unit can be expanded or contracted - this is normally most useful for the display.
Current origin:	Normally this is the lower left corner of the sheet, but it can be altered, which shifts the whole picture as all co-ordinates are expressed relative to it.
Current position:	For the plotter this is simply where the pen would be if all previous commands were obeyed exactly, i.e. it may be off the sheet even though plotting off the sheet is suppressed. For the display it is more complex but is basically where the pen would be if the display were a plotter. In both cases it is expressed in current units relative to the current origin.

In Section 4, the following terms are also used:

Data area:	This is an area inside the sheet, inside which data points are to be plotted. There can be several data areas on one sheet. Points outside the data area are suppressed.
Data units:	The units in which data is expressed before scaling, i.e. its natural units.
Scale:	The number of data units per current unit (different for each axis).
Datum:	The data values (in data units) at the lower left corner of the current data area.

<u>Plotter</u>

Use of the digital plotter is quite straightforward, as each routine either sets up parameters for later routines, or causes output of plotter instructions. Even if actual plotting is delayed by using pseudo-offline (POL) routines, the pen will eventually be driven in the exact order the instructions were generated by the program.

Display

The graphical display is not so straightforward as the picture has to be continually refreshed. Everything to be displayed is held in a display file (an array set up at the start of the program) in the form of items. Each item consists of code which has been generated by routines in the package and placed in a code buffer (another array which is set up for each item). However, items are not displayed until the code in the code buffer is inserted into the display file - this also releases the code buffer for further use. Although each routine in the package could create and insert an item in the display file thus causing the item to appear immediately and make the display unit behave more like a plotter, this would lose valuable facilities. Chief of these is the ability to build up and identify logically coherent parts of a picture into a single item which can subsequently be manipulated or changed without affecting other parts of the picture. Since this implies that items are not always displayed in the order they were created, the "current position" of the beam is not a useful concept unless the beam is moved to a known position at the start of each item. The routine GNITEM ensures this, and also allows an item to be moved about the screen without recreating it (GMOVIT).

The display package works entirely in vectors (relative displacements) except for the initial positioning command in GNITEM, so that full use can be made of the facility to include subpictures in an item. These subpictures have only one copy which is referred to repeatedly thus saving space with repeated shapes. There are two types of subpicture, simple (see GENTER) and complex (see GDEFSB et al.). A simple subpicture is held in a code buffer and cannot be changed while any item in the display file refers to it. A complex subpicture consists of one or more items and is set up in the display file but is not actually displayed until an item calls it. However, items comprising the subpicture may be freely manipulated or modified while the subpicture is being displayed. Both types may be nested but in practice this is most useful for complex subpictures - conversely unnested subpictures are more efficiently handled as simple subpictures.

The other distinctive features of the display is the ability to interact with the program using either a light pen or sense keys. In either case, a routine (GACT) exists which causes the program (but not the display) to halt until some specified action is taken. This action can then be examined and the display altered appropriately.

The light pen can be used in two ways. First, it may be used to point to a particular item which can then be identified within the program. Alternatively, a tracking cross can be moved around the screen using the light pen, and its co-ordinates determined. Apart from the sense keys on the display unit itself, the sense keys on the operator's console may also be examined, but changing them does not constitute an action for GACT.

Method of Use

Although most programs will be designed from the start either for the plotter or for the display, the device used is not determined until the program is loaded. Most of the routines are held in the ordinary Fortran library under useridentifier FOR OBJ and are fetched automatically. Those specific to a particular device, including GSTART which must always be called, are held on the system disc under useridentifier PLOPAC for the plotter and DISPAC for the display. By assigning channel 3 to one of these before compilation or loading, the appropriate routines will be fetched, e.g.

```
&JOB; AUSER; PLOTTER PROGRAM;
&ASSIGN; 3; DC; 0; ANYTHING, PLOPAC;
&FORTRAN; L;

          <plotter program>

&RUN;

          <data>

&END;
```

or

```
&JOB; BUSER; DISPLAY PROGRAM;
&ASSIGN; 3; DC; 0; ANYTHING, DISPAC;
&LOAD; DISPROG, BUSER; DC; 6; FORTRAN;
&RUN;
&END;
```

With the plotter, the operators can decide at run time to direct all plotter output to disc to be plotted later. Normally this makes no difference, but if a program requires special setting up of the pen, or changes in pen colour, there will be no way the operators can tell when this should be done. Thus the operators must be informed beforehand so that the program can be run with the plotter used directly.

With the display, large programs may have to use DES1, in which case the console on which input can be typed for GACT is the operator's console. Smaller programs will run under DES2, in which case the remote console beside the display unit is used. Since under DES2 the card reader may be in use, the Batch system has been modified so that jobs can be run from a disc-file instead of cards. This is done by typing BATCH,DC. instead of BATCH. after which the logical volume number of the disc and useridentifier and filename of the file must be supplied. Such files contain images of the commands that would have been on cards (cf REMJOB in KOS). For further details, see the specification of SPIDIB.