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The Use of a Micro-Computer as an Aid to Theoretical Calculations*

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Ways in which 'micro-' or 'personal' computers can be used to assist energy calculations for conjugated systems are discussed, using as an example programs written in the high-level language BASIC applied to simple Hückel theory. The aim of the work is to develop short, easily understood, routines which can be used in a flexible way, especially by the occasional user who lacks ready access to large computing facilities.

INTRODUCTION

A variety of relatively inexpensive small computers have become available in recent years. These provide new opportunities for carrying out calculations which are very laborious to do by hand, yet which do not always justify the use of time on expensive large computers.

This paper summarises some experiences of (BASIC) program writing in one such area; that of simple Hückel theory. Details of individual programs may be obtained from the author, and are described more fully elsewhere[1].

COMPUTER EQUIPMENT

A standard small North-Star Horizon computer was used. This was fitted with 24K of random access memory, two single sided double density disc drives, a Lear-Siegler ADM 3A Visual Display Unit, and a Teletype 43 printer. The North-Star Disc Operating System (Release 5.0) was used to support programs written in North-Star BASIC, with arithmetic precision of 8 significant figures. These can quite easily be translated into other dialect versions of BASIC, for use on other machines.

The high level computer language BASIC has been severely criticised[2], but it remains useful; it is widely available, even though in a number of slightly different dialects; it is easy to understand; and it is a convenient language for the rapid and flexible construction of short programs for particular purposes. High machine speed and efficiency are sometimes of less importance than availability of the computer for many different tasks with minimum programming effort.

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The use of disc drives for data storage, as described here, is not essential. It is estimated that programs of the same capacity (and greater speed once loaded) could be written for computers using tape storage if approximately an extra 8K of internal memory was available. (1K represents 1024 bytes of memory; each byte has 8 bits for most small computers at present.)

TYPES OF CALCULATION, AND METHODS

The fundamental quantities sought within Hückel Theory are the energies of the (LCAO) molecular orbitals, and the sets of LCAO combinatorial coefficients. For a given structure these are given by the eigenvalues and the eigenvectors, respectively, of the structure's adjacency matrix **A**. Alternatively, the Hückel energies (eigenvalues) can be derived as the roots of the polynomial which is represented by the determinant $|\mathbf{A} - x\mathbf{I}|$.

Derivation of the polynomial $|\mathbf{A} - x\mathbf{I}|$ can be done with the aid of some of the well known factorisation schemes[3–5]. These are especially useful now that such techniques have been extended to heteroconjugated systems[6,7]. The method involves expressing the required polynomial as a function of simpler known ones, for arithmetic manipulation of polynomials by computer can be done very simply (PROGRAM 1). Two PROGRAMS (2 and 3) enable the roots of the required polynomial to be isolated once its coefficients have been evaluated.

Most matrix methods[8–11] used for computer calculation convert the adjacency matrix **A** into a near diagonal matrix, in which the eigenvalues appear as the diagonal elements, and which has the same eigenvectors. One of the simplest methods, though not the fastest, is that of Jacobi, and a convenient BASIC implementation has been developed (PROGRAM 4). A second matrix method we have used is a modification of what is known as the Power Method (PROGRAM 5) which allows any eigenvector associated with a given known eigenvalue approximation to be calculated. This can save time when only a few of the roots are required, but as it is written it is only suitable for non alternant systems; it becomes unreliable when there is symmetry of eigenvalues.

An example of the application of these techniques is shown by an examination of the sensitivity of HMO models of the methylazulenes to variation of the Hückel parameters[12].

CONCLUSION

The modern generation of general purpose small computers are useful tools for performing calculations of medium complexity, and we have found that they give good results when applied to simple Hückel theory. Programs which have been written in BASIC for a limited, 24K (including the BASIC interpreter), memory space, can handle systems up to about 25 atoms (eigenvalues and eigenvectors) or considerably more if eigenvalues (Hückel energies) alone are required.

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SAŽETAK

Upotreba mikrokompjutera kao pomagala u teorijskim računima

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Razmatrane su mogućnosti upotrebe mikrokompjutera za račun energije konjugiranih sistema, koristeći kao primjer programe, pisane u BASIC-u, primijenjene na jednostavnu Hückelovu teoriju. Svrha rada bila je razviti kratke i lako razumljive rutine koje se mogu fleksibilno koristiti, posebno za neredovite korisnike koji nemaju jednostavan pristup većim računarskim sistemima.