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HMOVG: An Interactive Computer Program Based on the Hückel Molecular Orbital Model and Making an Extensive Use of Graphic Facilities *

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Abstract

HMOVG (*Hückel* Molecular Orbital Vector General) is basically a Hückel Molecular Orbital (HMO) program making an extensive use of interactive graphic facilities provided by a calligraphic display system. Most of the input is made from a data tablet and the output is treated graphically on the display monitor. This enables the user to enter by a rough drawing the system to be calculated and then to visualize interactively the HMO electronic structure and wave functions.

Computer graphics techniques are now widely used in a large range of chemical applications [1–5]. Indeed most problems in molecular structure and dynamics, conformational analysis and chemical reactivity should benefit from an adequate representation on a computer graphics equipment. The 3D visualization of molecular systems, interconversion processes and reaction mechanisms can be of great value to the chemist, in helping him estimating the chemical behavior, and ultimately the reactivity of the system.

In this laboratory, much work has already been devoted to the implementation of computer techniques in chemistry [6, 7], particularly in the field of computer graphics [5, 8]. We now have access to an interactive computer graphics system consisting of a PDP 11/60 minicomputer and a Vector General 3404 calligraphic display system (for a detailed description of the configuration, see ref. 5). Our main interest is to use this equipment in both fields of education and research in chemistry. Actually, our computer graphics project aims at developing applications in three different areas: (i) molecular modelling, making full use of the possibilities of the equipment to visualize 3D objects; (ii) representation of dynamic processes in molecules such as intramolecular rearrangements; (iii) visualization of molecular properties derived from quantum chemical calculations. In view of the difficulty for a non-specialist to analyze and interpret the results of such calculations, this last application is particularly important if one wishes to popularize the use of quantum chemical models. In this communication, we describe the first development we have made in this field.

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The simplest model of quantum chemistry is undoubtedly the HMO method [9]. This model, which treats only the π electrons of the system, is very successful in interpreting some physical and chemical properties of unsaturated organic compounds. This explains why the HMO model is still used nowadays in organic chemistry [10]. However, for large π systems, introduction of the system topology in the form of a connectivity matrix and analysis of the results coming out as a long series of numbers can be a time consuming task, not always exempt of errors. This prompted us to develop a computer program based on the HMO model, but using as much as possible interactive graphic devices for input and output.

Program description

The HMOVG program is made of seven overlayed parts: (i) the user terminal input/output (I/O); (ii) the graphic input; (iii) the geometry optimization; (iv) the HMO calculation; (v) for molecules with degenerate energy levels and of C_{nv} or D_{nh} symmetry, the construction of new eigenvectors respecting the molecular symmetry; (vi) the output on a printer-plotter and (vii) the graphic output on the display monitor.

The part dealing with I/Os on the terminal needs the user to answer a few short questions concerning program options. Then, the graphic input, made from a data tablet, allows the user to build the so-called Hückel connectivity matrix reflecting the topology of the π electrons system. The molecular geometry is simply entered through an approximate drawing (Fig. 1) of the π skeleton on the data tablet. The user can at every moment check his input by visualizing on the graphic monitor the echoed picture made of the bonds entered so far.

After the input, the geometry optimization program calculates the exact atomic coordinates of the planar π electrons system. To this end, the Hückel connectivity matrix is used as a starting point and algorithms have been developed which search for cycles and branchings in the molecule. All bonds are assumed to have the same length; bond angles are supposed to be 120° in a branching or the exact value in a cycle. In order to respect the

molecular configuration in a branching, a test is made from the approximate molecular drawing to determine whether three consecutive bonds are in cis or trans position. The HMO calculations are then performed by using a standard program with the QL algorithm for matrix diagonalization [11].

In cases of molecules with C_{nv} or D_{nh} symmetry, the program is able to build a new set of eigenvectors respecting the symmetry. To this end, the user has to specify, through the data tablet, the atoms defining the molecular mirror plane(s).

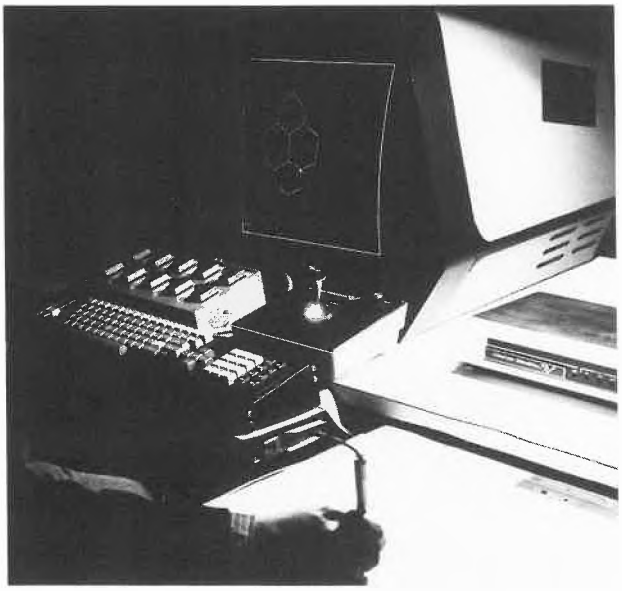

Fig. 1: The data tablet and the display monitor of the graphic equipment while entering the pyrene molecule.

We have previously developed a package of routines allowing to draw printer-plots on the line printer [5]. Optionally, HMOVG makes use of this package for producing a printer-plot of the molecular skeleton with atom numbering, a diagram of the Hückel energy levels and a schematic representation of any molecular orbital. In addition, a conventional listing of all the HMO results may also be obtained.

Most part of the informations provided by the results may be presented graphically in the form of a diagram of the energy levels for the π electrons with the corresponding electronic population and a representation of any molecular wave function. Each schematic orbital is made of π atomic lobes superimposed to the molecular skeleton and scaled in proportion to their weight in this orbital, one half of the lobe being hachured according to the sign of the corresponding component (Fig. 2). This graphic output makes use of the interactive I/O devices. Using several potentiometers, it is possible to scale the whole picture or the molecular orbital schematic drawing and to rotate or translate the molecule. In addition, for

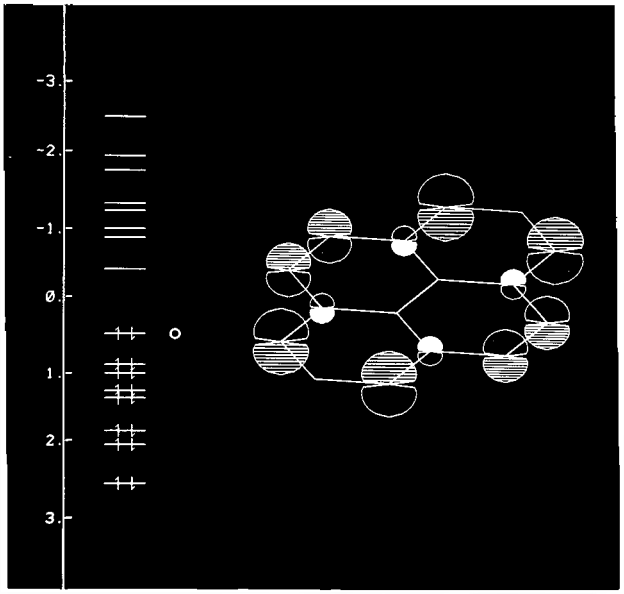

Fig. 2: The monitor displaying the electronic energy levels and the highest occupied molecular orbital of pyrene.

aesthetic reasons, it can be useful to uniformly scale the π lobes and this is made possible through another dial. In order to avoid the problem of 3 D lobes, we have chosen to represent 2 D lobes which are always bound to stay in the xy plane of the display [12], independently of the molecular rotation, our 2 D π lobe being a geometrically correct representation only when the molecule is located in the yz plane. Finally, the cursor echoed on the screen allows to select through the data tablet any other molecular orbital to be represented.

Since this program is in use in our department, it has proved to be very useful and convenient through its interactive graphic capabilities. Indeed it can readily be used by chemists without any prior knowledge of computer science, since all the graphic I/Os are self-explanatory. The next step in this project will be to develop similar interactive graphic programs for more sophisticated molecular orbital models and work in this direction is in progress.

The program has been written in FORTRAN and runs under the operating system RSX-11 M. A listing of the program with instructions for its use is available upon request. However, the reader should be aware that the graphic part of the program makes full use of the particularities of the graphic software.

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12 Conventionally the x axis is chosen as the horizontal axis of the display, whereas y is the vertical one; z is thus the 3D depth axis.