

HMO version 1.1: A Huckel Molecular Orbital Program for the Macintosh

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***Abstract:** HMO version 1.1 performs Huckel molecular orbital calculations on the Macintosh computer for structures containing up to 100 atoms. The program is interactive and simply requires that the structure of the target molecule be drawn and the number of π electrons be specified. The program automatically constructs the secular determinant from the supplied structure and computes the eigenvectors and eigenvalues by the Jacobi diagonalisation method. The program can accommodate various heteroatoms in the calculation. The output of the program can be displayed in graphic and tabular form. The executable program is included on disk.*

INTRODUCTION

HMO version 1.1 performs Huckel molecular orbital calculations on the Macintosh computer for structures containing up to one hundred atoms. The program is highly interactive and simply requires that the structure of a target molecule be drawn with the mouse by selecting any desired rings or heteroatoms from a palette (Fig. 1). The program automatically constructs the secular determinant from the supplied structure and computes the eigenvectors and eigenvalues by the Jacobi diagonalisation method.¹ The output of the program can be displayed in both graphic and tabular form and includes the empirical formula, number of atoms, number of π electrons, secular determinant, eigenvalues, total energy, delocalization energy, delocalization energy per π electron, eigenvectors, charge densities, total charge, electron density - bond order matrix, electrophilic, radical, and nucleophilic superdelocalizabilities,³ free valences, elapsed time for matrix diagonalization, total elapsed time, energy level diagram, and eigenvector diagrams.

The program has the capability of performing calculations on structures that contain heteroatoms. The heteroatom parameters include the resonance integrals, coulomb integral, valence, and symbol. The calculations can be performed using either a default set of built in parameters or user defined parameters. The default set of parameters are those suggested by Van-Catledge.⁴

The program, when operated in a Multifinder environment, will execute calculations in the background thus allowing the user to operate other programs while a lengthy calculation is in progress.

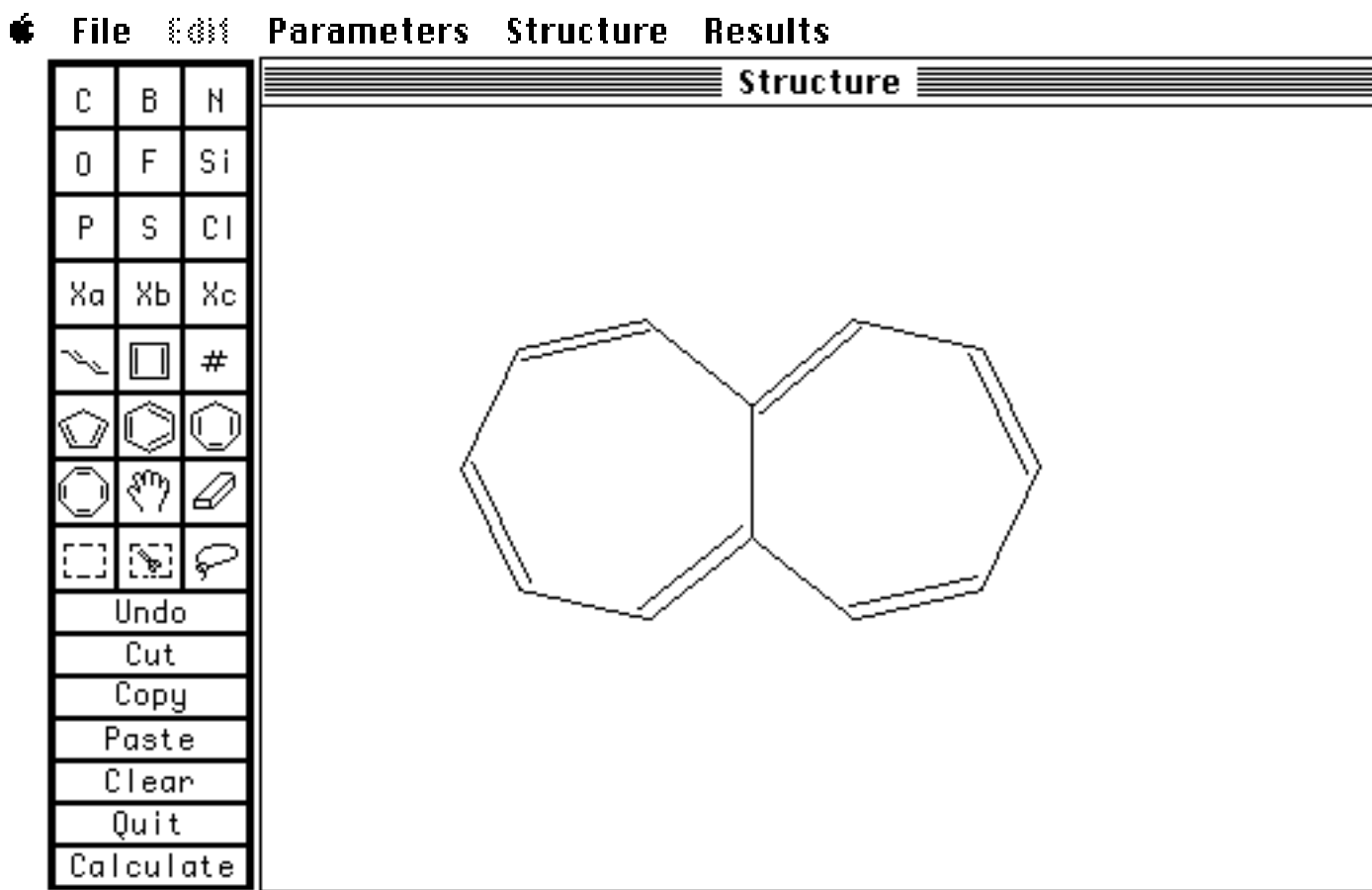


Fig. 1. The palette, menu bar, and drawing window of HMO 1.1.

DETAILED DESCRIPTION OF PROGRAM OPERATION

HMO 1.1 has been designed to be consistent with the Macintosh User Interface Guidelines⁵ and will therefore present a familiar environment to experienced Macintosh users. Like many graphically based Macintosh applications the program commands are divided between those located in the menus and those in the palette. A detailed description of the available commands will follow.

The Menu Commands

The Apple Menu

Help...

A window appears containing the title of this program and related information. Pressing the "Help" button allows the user to scan through several screens containing an abbreviated description of some of the program's features.

The File Menu

Open...

This command allows a previously saved structure document to be loaded from a disk file and displayed in the "Structure" window. The user may select the desired structure document from the scrollable portion of the dialog box and either double clicks on the item or presses the "Open" button. If the "Structure" window already has contents when a new structure is opened, the new structure will be added to the window and it will be selected; it may then be positioned to a different screen location as desired. HMO structure documents may also be opened from within Finder by double clicking the document icon.

Close

This item closes the current "Calculation Results" window. It is equivalent to using the close box of that window.

Save as...

The exact title of this menu item will depend on which window is foremost. When the "Structure" window is in front, the menu item will read "Save Structure as...". Choosing this item brings up a dialog box in which the user can request to save the current structure either as a HMO structure document that can later be opened by HMO, or as a PICT document that can be opened with a drawing program such as MacDraw. In either case, the user is prompted to name the file being saved and presses the "Save" button or the return key to actually save the file. When the "Calculation Results" window is foremost, the menu item will read "Save Calculation as..."; the current calculation results can be saved as a text document that can later be opened by a text editor or word processor. When the "Energy Level" window is foremost, the menu item will read "Save Energy Levels as..."; the energy level diagram is saved as a PICT document. When the "Eigenvectors" window is foremost, the menu item will read "Save Eigenvectors as...". The eigenvector diagrams can be then saved as a series of numbered PICT documents.

Page Setup...

This menu item gives the standard Macintosh Page Setup Dialog.

Print...

The contents of all windows open at the time this command is chosen will be printed. Both the graphic and the tabular output can be printed. When printing the eigenvector diagrams, a built-in algorithm is used that allows the maximum number of diagrams to be printed per page depending on the selections made in the Page Setup Dialog.

Quit

Exits the program. The identical item in the palette serves the same purpose.

The Edit Menu

This is the standard Macintosh Edit Menu; it will be active only when there is text available to be copied to the clipboard or when a desk accessory is active. The editing commands available for structure manipulation are located in the palette.

The Parameters Menu

Parameters for a particular atom include the resonance integrals, coulomb integral, valence, and symbol. The calculations can be performed using either a default set of built-in parameters or user defined parameters. The default set of parameters are those suggested by Van-Catledge⁴ and are derived from semiempirical calculations. These parameters were chosen as the default parameters since they comprise a particularly complete set that includes various heteroatom-heteroatom resonance integrals.

Save Parameter File...

At any time, the current parameter set may be saved as a disk file that can later be opened by the program. Choosing this item gives the standard file dialog box where the user is asked to name the file being saved. The user then presses the "Save" button or the return key.

Load Parameter File

The current parameter set may be replaced with one contained in a disk file by choosing this item. The user selects the desired parameter file from the scrollable portion of the dialog box and either double clicks on the item or presses the "Open" button. The electronic portion of this paper contains two additional incomplete parameter set files that have been extracted from a series of papers by Hess and Schaad⁶ and from Streitwieser's classic work.⁷

Revert to Default Parameters

Choosing this item will revert the current parameter set to the default set.

The Structure Menu

Any item chosen from this menu will only effect the appearance of the structure on the screen and will have no effect on the calculation.

Reduce or Expand

The size of the structure may be increased or decreased by the chosen percentage. If no portion of the structure has first been selected with any of the selection tools, these commands will apply to the entire structure; if, however, a portion of the structure has first been selected, then these commands will only effect the selected portion of the structure.

Reflect Horizontal or Vertical

The orientation of the structure may be changed by a reflection in either the X or Y plane. If no portion of the structure has first been selected with any of the selection tools, these commands will apply to the entire structure; if however, a portion of the structure has first been selected, then these commands will only effect the selected portion of the structure.

Smooth bonds

Choosing this menu item may improve the appearance of a poorly drawn structure.

Rubber band

When the "Rubber band" item of the "Structure" menu is unchecked, a bond is constructed by clicking the mouse button on each end of the bond and a multiple bond is constructed by clicking on each end of the existing bond. Alternatively, if "Rubber band" is checked, bonds are created by clicking on one node and dragging to another. Although single bonds may be incorporated into a structure, they will, nevertheless, be treated as if they are part of the π system.

Fixed bond length

When this menu item is checked, all bonds will be drawn with the same default bond length. The default bond length is defined by choosing the next menu item.

Set default length...

A dialog box is presented in which the default bond length can be defined.

The Results Menu

This menu becomes active after a calculation has been performed. The various calculated indices will be displayed in color on machines equipped with a color monitor and configured to display color.

Energy levels...

Choosing this menu item presents a window that displays the calculated energy level diagram (see Fig. 2). The scale on the right of the diagram is calibrated in units of β . The electrons occupying the orbitals are shown as small dots. The maximum number of energy levels with the same energy (degenerate) that will be shown in the diagram is three.

Pi Bond Orders

If the "Structure" window is the front window, this menu item labels the bonds of the structure with the pi bond orders.

Charge Densities

If the "Structure" window is the front window, this menu item labels the atoms of the structure with the charge densities.

Superdelocalizabilities³

If the "Structure" window is the front window, these menu items will label the atoms of the structure with the chosen superdelocalizability. The electrophilic, radical, and nucleophilic superdelocalizabilities are useful reactivity parameters for determining the site of reaction of carbonium ions, radicals, and carbanions, respectively.

Free Valences

If the "Structure" window is the front window, this menu item labels the atoms of the structure with the free valences.

Eigenvectors...

This menu item opens a scrollable window containing a graphic display of the eigenvectors in which the dark circles indicate positive coefficients and the diameter of a circle is proportional to the square of the coefficient (the electron density) of the atom in that particular MO (see Fig. 3). These diagrams can be printed or saved as PICT documents. The PICT documents can be opened and further modified with a drawing program such as MacDraw.

HOMO

The scroll bar of "Eigenvectors" window is positioned to display the highest occupied molecular orbital (HOMO).

LUMO

The scroll bar of "Eigenvectors" window is positioned to display the lowest unoccupied molecular orbital (LUMO).

Tabular Results...

This menu item opens the "Calculation Results" window if it has been closed, otherwise it simply makes it the front window.

Clear Labels

Removes any calculated indices and atom numbers from the structure display.

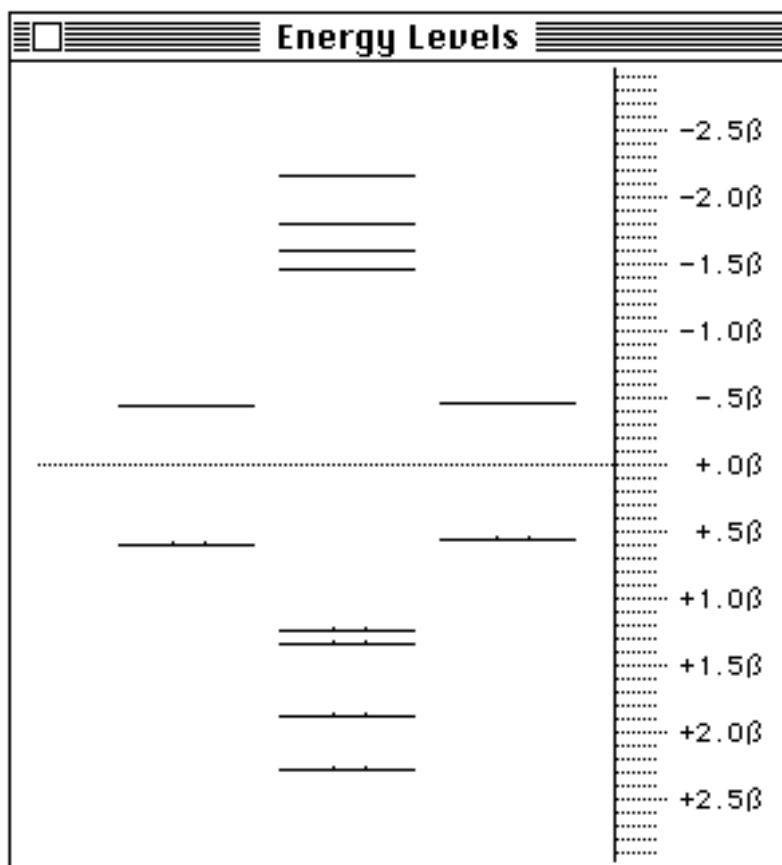
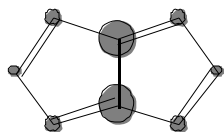
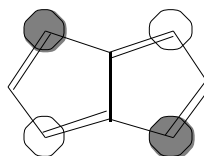


Fig. 2. A typical example of an energy level diagram generated by the program. This diagram is for heptafulvalene.

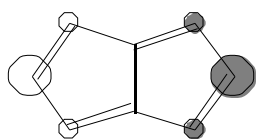
Eigenvector #2.3429



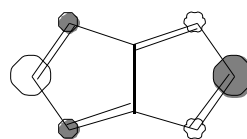
Eigenvector #1.0000



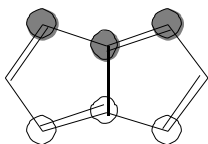
Eigenvector #1.4142



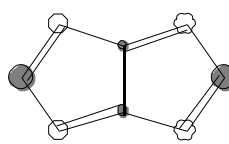
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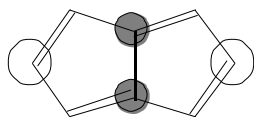
Eigenvector #1.000



Eigenvector #1.8136



Eigenvector #1.000



Eigenvector #2.000

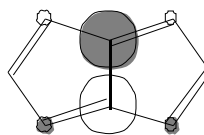


Fig. 3. An example of the eigenvector diagrams produced by HMO. This example shows the eigenvectors of pentalene. The diagrams depict a view of the eigenvector down the Z axis where the dark circles indicate positive coefficients and the diameter of a circle is proportional to the square of the coefficient.

The Palette Commands

Adding Heteroatoms and Editing Parameters

Heteroatoms are added to the structure by choosing an atom from the palette and then clicking on a node. Hold the option key down to continually add the same atom to a structure. To change an existing heteroatom, replace it with another choice from the palette.

Parameters for a particular atom include the resonance integrals, coulomb integral, valence, and symbol. A default set of parameters is provided for C, B, N, O, F, Si, P, S, and Cl.⁴ At any time, the current parameter set can be edited and then saved as a disk file. The parameters defined for a particular atom can be visualized by holding the command key down and choosing an atom from the palette. A window will appear that contains the parameters defined for that element (see Fig. 4). These parameters can be changed as desired. For certain elements (N, O, P, and S) radio buttons are used to toggle between atoms that provide one electron to the π system (such as the N in pyridine) and those that provide two electrons (such as the N in pyrrole). An altered parameter set can be saved as a disk file (see above) that can later be opened and used.

Three additional undefined atoms (Xa, Xb, and Xc) are provided which may be assigned parameters by the user. When one of these unspecified atoms is chosen that has not been previously defined, the parameter editing dialog box will appear into which the user may enter the desired parameters.

Resonance Integrals	
N.-C	1.02
N.-B	.66
N.-N	1.09
N.-O	.99
N.-F	1.14
N.-Si	.8
N.-P	.78
N.-S	.81
N.-Cl	.83
N.-Ha	.78
N.-Hb	.77
N.-Hc	0

N. N:

Coulomb Integral: .51

Valence: 3

Symbol: N

Cancel

Accept


Fig. 4. The dialog box that contains the parameters for nitrogen. Note that in the upper right hand portion of the dialog box, radio buttons are provided that allow the display to toggle between parameters for nitrogen that contribute one electron to the π system and those that contribute two.

Drawing Rings

To create a new ring, choose the desired ring size from the palette. Draw one of the ring bonds and then click on either side of the bond to determine the direction that the new ring will be drawn. To fuse a ring onto an

existing bond, choose the desired ring size, click on the ends of the bond (or if "Rubber band" is chosen, click on one node and drag to the other), and then click on the side on which the ring is to be drawn. To draw rings that contain only single bonds, hold the option key down before the third mouse click. A chain of atoms is constructed in a similar manner with the exception that the user is first prompted to enter the number of bonds desired. Although rings can be drawn that contain single bonds, these bonds will, nevertheless, be treated as if they are part of the π system.

Displaying Atom Numbers

To label the nodes with the atom numbers, press the number icon {  } of the palette.

Deleting Bonds and Atoms



To delete a bond, choose the eraser from the palette and click on the bond to be removed. Clicking on an atom will remove that atom and all attached bonds. When all bonds to a particular atom are deleted, the atom will also be deleted. Hold the option key down to use the eraser multiple times. A group of atoms may be deleted at one time by first selecting the atoms with the lasso or selection rectangles and then using clear from the palette.

Selecting and Moving the Structure



A portion of the structure may be selected using the selection rectangles or the lasso tools. Using the selection rectangle with the scissor icon will select a portion of the structure and simultaneously sever any bonds that intersect the selection rectangle. To move the structure to another screen location, choose the hand icon from the palette, move the hand cursor to the drawing window and drag the mouse with the button held down. A portion of a structure can be moved by selecting it, moving the cursor within the selection, and dragging.

Palette Editing Commands

Undo

Choosing Undo from the palette will sequentially remove bonds in reverse order (*ie.* the last bond added will be the first to be removed).

Cut

The contents of the "Structure" window or the selected portion of the structure are cleared from the screen and placed in the Clipboard.

Copy

The contents of the "Structure" window or the selected portion of the structure are placed in the Clipboard.

Paste

The contents of the Clipboard are placed on the "Structure" window (it is also possible to paste the contents of the Clipboard into other types of programs such as a word processor or drawing program).

Clear

The contents of the "Structure" window or the selected portion of the structure are removed from the "Structure" window.

Quit

Exits the program. The user is not prompted to save the current calculation. The identical menu item serves the same purpose.

If no portion of the structure has first been selected with any of the selection tools, the editing commands Cut, Copy, and Clear will apply to the entire structure; if a portion of the structure has first been selected then these commands will effect only the selected portion of the structure.

Performing the Calculation

Calculate (the return key is an equivalent)

This command brings up a dialog box showing the expected number of π electrons in a edit field. The user may change the number, if desired, at this time. Pressing the OK button or return key begins the calculation. The progress of the calculation is monitored in a window containing an advancing scale. When the calculation has been completed, a scrollable window titled "Calculation Results" will appear that contains the output of the program in text form. When Multifinder is active, the calculations can be performed in the background. Under these conditions, the user will be able to operate other programs while a calculation is in progress. At any time, a calculation can be aborted by holding down the command key and typing a period (.).

RESULTS AND DISCUSSION

Fig. 5 shows the results of some timing experiments using a Mac+ and IICI models. The calculations were performed on a series of linear polyenes of different length. The graph shows the relationship between the time needed to complete matrix diagonalization and the chain length. As expected, the time needed to do the calculation is approximately a function of the cube of the number of atoms. Furthermore, there is an obvious improvement in execution time using the more powerful IICI model, and one should anticipate further gains in speed with future improvements in hardware. As is readily apparent, the ability to perform calculations in the background under Multifinder is advantageous, particularly for large π systems, since this will give the user the opportunity to operate other programs while a calculation is in progress.

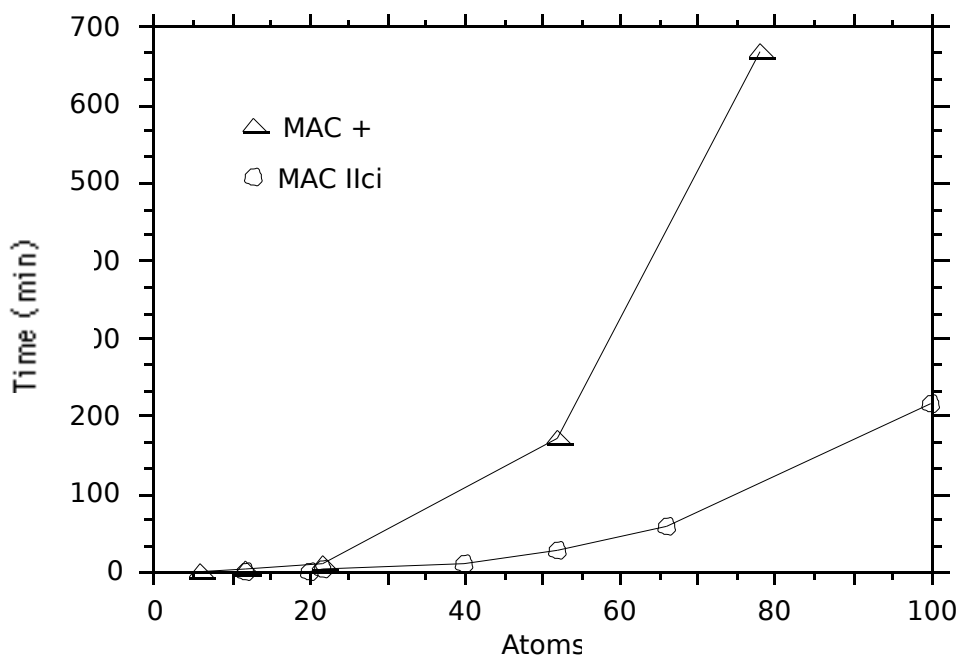


Fig. 4. Relationship between chain length and the time needed to complete matrix diagonalization for a series of linear polyenes. The calculations were performed with the MAC + and MAC IICI models.

EXPERIMENTAL

HMO was written with the Zbasic 5.0 compiler.² It has been tested on the Mac +, SE, SE30, II, and IICI models. When operating in a Multifinder environment, 525K of ram is reserved for the program. Included on the electronic portion of this paper is the executable program HMO version 1.1, a number of HMO structure documents, and additional parameter set files.

REFERENCES

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