

Since the original description of HMO 1.1 was published [Wissner, A. Tetrahedron Computer Methodology. **1990**, 3, 63-71], a number of modifications and improvements have been made; these are described herein. The current version of the program is HMO-plus 2.0

Changes to HMO-plus version 2.0

1. The program will now display a graphic representation of the molecular orbitals that are constructed using Slater type atomic orbitals (STOs) [J. C. Slater, Phys. Rev., 1930, 36, 57 ; K. B. Wiberg, "Physical Organic Chemistry", Wiley, 1964, pgs 25-26, 469-471]. Normalized STOs for $2p_z$ and $3p_z$ valence orbitals have the form:

$$\phi = N z r^{n-2} e^{-K r}$$

where N and K are constants that depend on the particular element and are calculated using simple rules derived by Slater. The constant N also includes the normalization factors. For a point in space, r is the distance of nucleus to this point and z is the distance of the point along the axis of the p_z orbital; n is the principle quantum number; for the atoms supported by the program, n has the value 2 or 3.

The actual STO formulas used are listed in Table I. All elements for which default parameters have previously been provided are supported with an STO. For user defined atom types, the program will attempt to use the most appropriate STO formula otherwise the STO for carbon will be used. Distances used with these STO equations are expressed in angstroms.

Table I. Normalized STOs for distances in angstroms.

atom	type	STO
C	$2p_z$	$3.590 z e^{-3.070}$
O	$2p_z$	$8.326 z e^{-4.300}$
N.	$2p_z$	$5.663 z e^{-3.686}$
B	$2p_z$	$2.055 z e^{-2.458}$
O: (O+)	$2p_z$	$10.020 z e^{-4.631}$
N: (N+)	$2p_z$	$7.020 z e^{-4.017}$
F	$2p_z$	$11.625 z e^{-4.915}$
S: (S+)	$3p_z$	$7.397 z r e^{-3.655}$
S.	$3p_z$	$5.953 z r e^{-3.434}$
Cl	$3p_z$	$8.825 z r e^{-3.844}$
P.	$3p_z$	$3.814 z r e^{-3.025}$
P: (P+)	$3p_z$	$4.880 z r e^{-3.245}$
Si	$3p_z$	$2.290 z r e^{-2.614}$

The MO wave functions have the familiar LCAO form:

$$\Psi_i = \sum_{j=1}^{\text{atoms}} c_{ij} \Phi_j$$

which after substituting the STOs becomes:

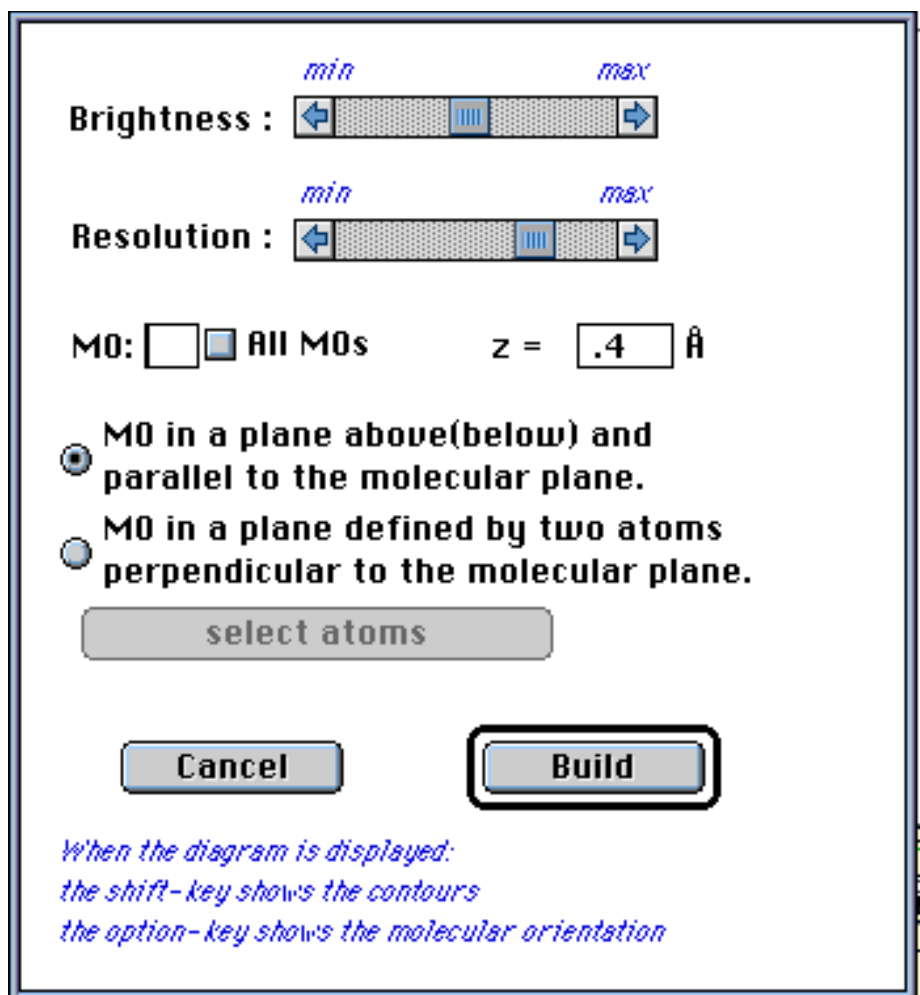
$$\Psi_i = \sum_{j=1}^{\text{atoms}} c_{ij} N z r_j^{n_j-2} e^{-K r_j}$$

This equation is used to build the π -MO diagrams. In constructing the diagrams, it is assumed that the molecule is planar. The screen coordinates are converted to cartesian coordinates by first finding the average bond length of the molecule in screen coordinates and then equating this average to 1.40 Å.

Attempts to use the above equation in analytic form to calculate the π -MO diagrams proved to be extremely slow on a MAC IIci, even to the extent that the calculation was not practical. This problem results from the large number of exponential terms that have to be evaluated at each region of space. In order to address this, the STOs are pre-calculated for distances up to 6.0 Å in units of 0.01 Å.; the resulting numeral data is then stored in the program and is retrieved from a look-up table as needed to generate the diagrams.

π -MO diagrams are constructed by the program that show a view of the MO in a plane located above or below and parallel to the molecular plane. The user can specify the distance of the plane along the z axis (positive z is above and negative z is below the plane); the default value of 0.4 Å is usually a good choice and is close where the wave function has a maximum values (see dialog box below).

A diagram can also be constructed that shows a view of the MO in a plane that is defined by any two atoms and is perpendicular to the molecular plane. The defining atoms can be chosen graphically by using the "select atoms" button (see dialog box below). Because the orientation of the molecule will change when this type of diagram is created, the orientation of the molecule and the relative placement of the plane can be visualized by holding down the option key. A scale, calibrated in angstroms, will also appear. In fact, this type of diagram is not restricted to a plane defined by two atoms of the molecule. By making use of dummy atoms, any plane perpendicular to the molecular plane can be used. In order to define this plane, activate the structure window after a calculation has been completed. Draw a new bond which will be used to define the plane; the dummy atoms created by this bond can be chosen as the atoms which define the plane. In doing so, they will not effect the diagram in any other way.



In both types of diagrams, a positive value for the wave function is colored blue while a negative value is colored red. The brightness of the color in a given region is proportional to the magnitude of the wave function in that region. Pure black would indicate that the function has a zero value.

HMO-plus will also perform a population analysis of the π -electronic distribution. For a point in space, the π -electron density is given by:

$$2 \sum_u^{\text{occ}} \Psi_u^2 = \mathcal{P}(x) = \sum_{i=1}^n \sum_{j=1}^n P_{ij} \Phi_i \Phi_j$$

where again we use normalized STOs for the atomic orbitals Φ_j and the factors, P_{ij} , are elements of the bond order - electron density matrix. The summations in the right-hand formula are over all atomic orbitals. This equation can be expanded to give:

$$\mathcal{P}(x) = \sum_{i=1}^n P_{ii} \Phi_i \Phi_i + \sum_{i \neq j}^n \sum_{j=1}^n P_{ij} \Phi_i \Phi_j$$

The first term in the expanded formula represents contribution of the atom centered population to the total π -electron density while the second term gives the bond centered population. HMO-plus will provide diagrams for the total π -electron density distribution as well as separate diagrams for the atom centered and bond centered distributions.

These diagrams depict a view of the π -electron density in a plane located above or below and parallel to the molecular plane. The user can specify the distance of the plane along the z axis. The electron cloud is shown in blue where the brightness of the color is proportional to the magnitude of the electron density in that region.

A π -electron density difference map can be constructed based on the formula :

$$\Delta P(x) = \sum_{i=1}^n n_i \Phi_i \Phi_i - \sum_i P_{ii} \Phi_i \Phi_i$$

This map is a graphical representation of the difference between the molecular atom-centered population and the π -electron density in the corresponding isolated atoms placed at those positions which they occupy in the molecule. The resulting diagram is a pictorial representation of the charge density within the molecule. A negative density will be shown in red and a positive density in blue. In the above formula n_i is the number of electrons contributed to the π -system by atom i .

Before any of these diagrams are created, the user is presented with a dialog box containing scrolls bars that control the overall brightness and the resolution of the diagrams. The default setting for brightness is usually sufficient. The brightness control has no effect on the speed of creation of the diagram. With respect to the resolution of the diagrams, there is a significant time penalty for the higher resolution settings.

For any of the above types of diagrams, the π -MO or electron density contours can be displayed by holding down the shift key; these contours are displayed as a series of randomly color bands where the width of a band is a measure of the rate of change of the wave function or electron density, respectively, in the region of space considered. In addition, with any of the above diagrams, when the cursor is placed within the window containing the diagram and the mouse button is held down, the numeral value of the wave function or electron density at the point indicated by the cursor will be displayed until the button is released.

These diagrams require systems operating with 32bit Quickdraw and best results are obtained when 256 colors are chosen from the Monitors control panel. As is the case with all the graphics generated with HMO-plus, these diagrams can be printed (in color or B&W), saved as PICT files, or copied to the clipboard.

About 30K of ram is needed for each color diagram held in memory; in addition, a 500K off screen buffer is temporarily allocated for construction of the diagrams. Because of these

memory requirements, no color diagrams can be constructed when the program is configured to run at the recommended minimum memory setting. If possible, the program should be operated at the preferred setting or greater (the memory requirements of the program can be changed by choosing "Get Info" from within Finder).

2. HMO-plus will now execute self-consistent field (SCF) calculations using what is commonly referred to as the Pariser-Parr-Pople approximation (PPP-SCF) [R. Pariser, R.G. Parr, J. Chem. Phys., 1953, 21, 466, 767; J.A. Pople, Trans. Faraday, Soc., 1953, 49, 1375]. The PPP-SCF calculations, as implemented in HMO-plus, are for closed shell systems only without configuration interaction (CI). A full discussion of PPP-SCF theory will be avoided here although the parameterization scheme used will be addressed; the user is referred to the following discussions of PPP-SCF theory : R.L. Flurry, Jr., "Molecular Orbital Theories of Bonding in Organic Chemistry", Marcel Dekker, Inc., New York, 1968; L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W.A. Benjamin, Inc., New York, 1966; M.J.S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw Hill, Inc., New York, 1969.

As implemented by HMO-plus the diagonal elements (F_{ii}) of the Fock matrix are given by:

$$F_{ii} = U_{ii} + 1/2 P_{ii} \gamma_{ii} + \sum_{j (\neq i)} (P_{jj} - n_j) \gamma_{ij}$$

The off-diagonal matrix elements (F_{ij}) are given by:

$$F_{ij} = \left\{ \begin{array}{l} 0 \quad (i,j \text{ nonbonded}) \\ \beta_{ij}^{\text{core}} \quad (i,j \text{ bonded}) \end{array} \right\} - 1/2 P_{ij} \gamma_{ij}$$

where P_{ij} are elements of the bond order - electron density matrix, n_j is the number of electrons contributed to the π -system by atom j , β_{ij}^{core} are the core resonance integrals, γ_{ii}^1 are the one-center electron repulsion integrals, and γ_{ij}^1 are the two-center electron repulsion integrals.

The usual assumption is made that the coulomb integral parameter, U_{ii} , can be equated with the negative of the valence state ionization potential (VSIP) of atom i and that the one-center electron repulsion integrals, γ_{ii}^1 , are given by the difference between the ionization potential and electron affinity of atom i . The valence state data of Hinze and Jaffe are used to evaluate these quantities [J. Hinze, H.H. Jaffe, J. Amer. Chem. Soc., 1962, 84, 540]. These data can be edited by choosing an atom from the palette while the command-key is held down and then pressing the button "SCF-PPP"; the valence state data for the atom will then be

available to the user for modification. Radio buttons are presented that allow switching the data display for atoms that contribute one or two electrons to the π -system.

As pointed out by Sane and Sane (K. Sane, K. V. Sane, Indian J. Chem., Sect. A 1977, 15A(8), 740.), equating U_{ii} with the negative of the VSIP of an atom is a valid approximation only if the atomic orbital belongs to a non-orthogonal basis set. Since the an orthogonal basis set is assumed in the PPP method, a correction to the coulomb integral parameter is needed. Such a correction can optionally be incorporated into the parameterization scheme by activating the check box "**Use Sane correction**". U_{ii} will then be given by:

$$U_{ii} = -VSIP - s \sum_{\substack{j \text{ bonded} \\ \text{to } i}} \beta_{ij}^{\text{core}}$$

where s can be considered as the overlap integral but is used here as a constant parameter that is adjusted to give best agreement between the calculated and experimental ionization potentials. Correcting the coulomb integral parameter in this manner results in far improved predictions of ionization potentials (see below).

The two-center electron repulsion integrals can be evaluated either with the formula of Beveridge and Hinze [D.L. Beveridge, J. Hinze, J. Amer. Chem Soc., 1971, 93, 3107] or the formula of Nishimoto and Mataga [K. Nishimoto, N. Mataga, Z. Physik. Chem. (Frankfurt), 1957, 12, 335]. When performing a PPP-SCF calculation the user is presented with the option of choosing one or the other of these two formulas. With consideration of the other parameters used in this implementation and the lack of CI, it appears that use of the later formula gives better predictions of the ionization potential of molecules than the former (although these predictions are routinely too high unless the correction is applied to the coulomb integral parameter).

The formula for evaluating the core resonance integrals, β_{ij}^{core} , is given by :

$$\beta_{ij}^{\text{core}} = K_{ij} \left[a - \frac{b}{R_{ij}} \right]$$


where K_{ij} is the resonance integral parameter for atoms i and j that is used in the Hückel calculations and R_{ij} is the bond length between atom i and j . The quantities a and b are empirical parameters. By using the bond lengths for ethylene and benzene along with the respective empirical values for the core resonance integrals, the values $a = 0.988$ and $b = 4.62$ are found. The parameters a and b appearing in the above formula can be changed by the user by choosing the menu item " **β -core Integral Formula...**" from the "**Parameters**" menu. The resonance integral parameters, K_{ij} , were original derived employing PPP-SCF calculations [F. A. Van-Catledge, J. Org. Chem., 1980, 45, 4801] that use the Beveridge and Hinze [D.L. Beveridge, J. Hinze, J. Amer. Chem Soc., 1971, 93, 3107] parameterization

scheme which in turn uses the Ohno formula [K. Ohno, Theoret. Chim. Acta, 1964, 2, 219] for evaluating the core resonance integrals. Thus, the above formula for β_{ij}^{core} used by this program has the same $1/R$ dependence as the Ohno formula from which the K_{ij} parameters were originally derived. By using this scheme to estimate the core resonance integrals, no additional parameters other than **a** and **b** had to be incorporated into the program.

Unlike a simple Hückel calculation where the results depend only on the connectivity within the molecule and not its actual geometry, a SCF-PPP calculation requires input of atom-atom distances in order to determine the appropriate values for the various integrals. HMO-plus has been designed to make input of the molecular geometry fairly transparent to the user. The molecule, as drawn by the user, is considered to be planar. It is assumed that a linear relationship exists between the π -bond order and bond lengths of the form:

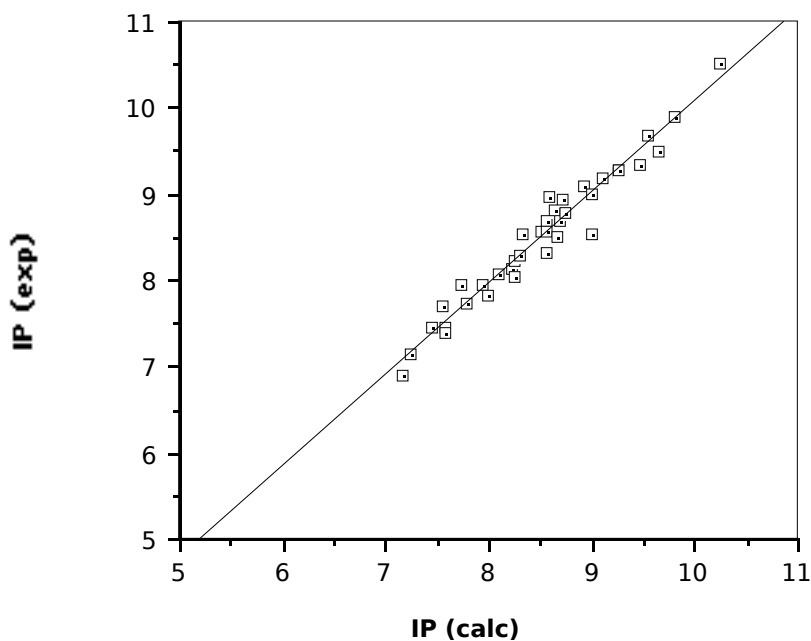
$$R_{ij} = k - hP_{ij}$$

where k and h are constants which depend on the atoms i and j . For the different types of hetero- and homo-nuclear bonds, a series of k and h values have been extracted from the literature or estimated from tables of standard bond lengths and incorporated as parameters to the program [(a) M.S. Dewar, G.J. Giecher, J. Amer. Chem. Soc., 1965, 87, 685. (b) I. Fisher-Hjalmars, S. Meza; Acta Chem. Scand., 1972, 26, 2991. (c) A. Skancke, P.N. Skancke, Acta Chem. Scand., 1970, 24, 23. (d) G. Hojer, S. Meza, M.E. Ruiz, Acta Chem. Scand., 1974, 27, 1863. (e) O. Gropen, P.N. Skancke, Acta Chem. Scand., 1970, 24, 1768. (f) W.J. Hehre et al J. Chem. Phys., 1970, 52, 2769]. The button entitled "**Bond order-bond length equations...**" located in the parameters window will allow the user to modify existing h and k values or add values for bond types that are not currently defined. From the initial π -bond orders obtained from the beginning Hückel calculation, the bond lengths can be calculated using these linear relationships; these lengths are then used, in turn, to derive the core resonance integrals and the two-center electron repulsion integrals. During each cycle of iteration, the bond lengths are recalculated from the new bond orders and these are used to reevaluate the integrals. The resulting calculation then is self-consistent for the variations of the integrals with bond length. This scheme for allowance of molecular geometry in hydrocarbons was previously adapted by Dewar and Giecher [M.S. Dewar, G.J. Giecher, J. Amer. Chem. Soc., 1965, 87, 685]. While the above scheme is useful for distances between bonded atoms, the longer range distances are evaluated using the geometry as drawn by the user and are not reevaluated for each iteration. To do this the screen coordinates must be calibrated to correspond to the cartesian coordinates; this is done by first finding the average bond length of the molecule in screen coordinates and then equating this average to 1.40 Å. It is therefore important to draw structures that, as far as possible, have equal bond lengths and reasonable bond angles so as to accurately depict these long range interactions.

Calculations can also be executed using a defined geometry such as the experimental geometry. This is accomplished by making use of the user defined atoms that are accessed using the  tool of the palette. Atoms can be defined such that k is equal to the actual bond length and $h = 0$ so that there would be no bond order dependence of the bond length. A sample HMO-plus document illustrating this is provided.

Although many aspects of the parameterization scheme implemented herein have been used before, the combination of these aspects are, in some ways, unique. In order to validate this parameterization scheme, a comparison of the calculated and experimental first ionization potentials has been made for a variety of hydrocarbons and heteroatom-containing molecules. The results of this comparison are shown in the graph and table below:

$$y = -0.52310 + 1.0591x \quad R^2 = 0.957$$



compound	IP (exp)	IP (calc)	difference
fulvene	8.55	8.52	0.03
benzene	9.24	9.26	-0.02
ethylene	10.52	10.26	0.26
trans-butadiene	9.07	8.94	0.13
hexatriene	8.23	8.26	-0.03
azulene	7.43	7.45	-0.02
acenaphthylene	8.02	8.27	-0.25
fluoranthene	7.80	8.01	-0.21
dimethylenecyclobutene	8.80	8.65	0.15
naphthalene	8.12	8.24	-0.12
anthracene	7.38	7.60	-0.22
phenanthrene	8.07	8.09	-0.02
tetracene	6.88	7.18	-0.30
pyrene	7.70	7.55	0.15
styrene	8.55	8.57	-0.02
biphenylene	7.95	7.75	0.20
biphenyl	8.27	8.32	-0.05
chrysene	7.71	7.80	-0.09
coronene	7.44	7.59	-0.15
perylene	7.13	7.25	-0.12
trans-stilbene	7.95	7.94	0.01
phenol	8.52	9.00	-0.48
aniline	8.32	8.58	-0.26
fluorobenzene	9.19	9.11	0.08
p-benzoquinone	9.68	9.56	0.12
anthraquinone	9.34	9.47	-0.13
chlorobenzene	9.00	9.01	-0.01
pyrrole	8.97	8.58	0.39
pyridine	9.28	9.27	0.01
pyridazine	9.90	9.80	0.10
pyrazine	9.27	9.27	0.00
pyrimidine	9.47	9.64	-0.17
quinoline	8.67	8.56	0.11
isoquinoline	8.53	8.35	0.18
furan	8.78	8.76	0.02
thiophene	8.92	8.73	0.19
cinnoline	8.51	8.67	-0.16
phthalazine	8.68	8.69	-0.01

Changes to HMO-plus version 1.5-1.7

1. The name of the program has been changed slightly to **HMO-plus** in an attempt to distinguish it from at least two other programs (one shareware and the other commercial) called

HMO; the "plus" designation is an indication that this program does more than just simple Hückel calculations.

2. The program now calculates and displays a π -electrostatic potential diagram. A simple point charge model is used. At any point in space, the π -electrostatic potential is the potential energy resulting from the force exerted on a unit positive charge by the π -electron charge of each atom of the molecule. In calculating the potential, it is assumed that the molecule is planar and that the charges are located at points corresponding to the atomic coordinates; the potential is calculated within the plane of the molecule by summing the contribution of each atomic charge to the potential energy (at any given point in space: π -electrostatic potential = $\sum q_i/d_i$ where the q_i is the π -charge and d_i is the distance of atom i to that point).

A positive potential is colored blue and a negative potential is colored red. The brightness of the colors are proportional to the magnitude of the potential. Pure black would indicate a zero potential. When the π -electrostatic potential diagram is requested using the command located under the Diagrams menu, the user is presented with a dialog box containing scrolls bars that control the overall brightness and the resolution of the diagram. The default setting for brightness is usually sufficient; it may have to be decreased for molecules bearing full charges or increased for molecules with charges of low magnitude. The brightness control has no effect on the speed of creation of the diagram. In setting the resolution of the diagram, there is a significant time penalty for the highest resolution setting.

While the option key is held down and the π -electrostatic potential diagram is located in the front window, the direction and magnitude of the π -dipole moment will also be displayed.

While the shift key is held down and the π -electrostatic potential diagram is located in the front window, the electrostatic potential contours will be displayed as a series of randomly color bands where the width of a band is a measure of the rate of change of the potential in the region of space considered.

This diagram requires systems operating with 32bit Quickdraw and best results are obtained when 256 colors are chosen from the Monitors control panel.

Changes to HMO version 1.4

1. The energy level diagrams generated with previous versions of HMO were restricted to the range $\pm 3\beta$. Version 1.4 removes this restriction. To see energy levels outside the range $\pm 3\beta$, place the cursor within the energy level window and drag up or down while holding the mouse button down; the energy level diagram will then scroll vertically.

2. The energy level diagram of previous versions of the program only displayed degenerate energy levels up to 3. Version 1.4 will show all the degenerate energy levels present.

3. In order to do calculations on Mobius systems, negative resonance integrals have to be used. Earlier versions of the program would not accept a negative value for a resonance integral. This has been corrected in version 1.4

4. A "Check valences" item has been added to the "Structure" menu. You can now turn valence checking on or off. This is useful if you frequently do calculations on certain polyhedra where the number of bonds attached to a node can exceed the normal valence of carbon.

5. Two items have been added to the "Structure" menu: "Read connection table" and "Write connection table". Structures can now be imported and exported to ChemDraw™ via connection tables.

6. A horizontal scroll bar has been added to the eigenvalue diagram window. This control now allows the size of the depicted electron densities to be varied relative to the structure.

7. Previous versions of the program allowed the results of a calculation to be saved either as text or as PICT documents; they did not allow the user to save a calculation as a document that could later be opened and viewed by the program HMO. This ability has now been added. The "**File**" menu has been modified to accommodate this new functionality as follows:

Open Calculation...: This command opens a previously saved calculation document.

Close Calculation: This command will close the currently displayed calculation. If it is a new calculation, the user is prompted to save the file.

Save Calculation...: The calculation is saved as a disk file.

Open Structure...: This command allows a previously saved structure template to be loaded from a disk file and displayed in the "Structure" window.

Close Front Window: The current active window is closed.

Save as... : The exact title of this menu item will depend on which window is foremost. For example, when the "Structure" window foremost, the menu item will read "Save Structure as..." ; the current structure will be saved as a disk file which can later be opened by HMO. The tabular results are saved as a text file and the various diagrams are saved as PICT files which can be opened with a drawing program such as Macdraw.

Page Setup... : Gives the standard Macintosh page setup dialog. The items in this dialog will determine how many of the diagrams can be fitted on a page.

Print... : The contents of all windows open at the time this command is chosen will be printed.

Quit: Exits the program. If a new calculation has been performed, the user is prompted to save it as a disk file. The identical item in the palette serves the same purpose.

8. The "**Results**" menu has been replaced by two new menus: The menu labeled "**Diagrams**" has menu items that allow the display of several types of diagrams of the calculation results. The new menu items include:

Charge density diagram... : A display of the π -charge densities is presented where a negative charge is represented by an open circle and a positive charge is represented by a filled circle. The diameter of a circle is proportional to the magnitude of the charge density. The horizontal scroll bar allows the diameter of the circles to be adjusted relative to the structure.

The charge density diagram also shows the magnitude and direction (relative to the screen) of the π -dipole moment. The π -dipole moments calculated by HMO are only approximate and depend on how the structure is displayed on the screen. The following procedure is followed: The average distance separating the bonded atoms of the screen representation of the structure is determined and equated to 1.4 Å. All bond lengths are then assumed to be equal to this average length. The dipole moment is then calculated as the vector sum of the charge distribution using this assumed geometry.

Free valence diagram... : A display of the free valences is presented where the diameter of a circle is proportional to the magnitude of the free valence. The horizontal scroll bar allows the diameter of the circles to be adjusted relative to the structure.

Superdelocalizability diagrams... : A display of the superdelocalizabilities is presented where a negative superdelocalizability is represented by an open circle and a positive superdelocalizability is represented by a filled circle. The diameter of the circle is proportional to the magnitude of the superdelocalizability. The vertical scroll bar alters the display to show electrophilic, radical, and nucleophilic superdelocalizabilities. The horizontal scroll bar allows the diameter of the circles to be adjusted relative to the structure.

π -Bond order diagram... : A display of the structure is presented where the thickness of the bonds depends on the calculated π -bond order (the relationship between thickness and bond order is not linear). The horizontal scroll bar controls the resolution of the diagram. The vertical scroll bar adjusts the contrast of the diagram.

Self-atom polarizability diagram... : A display of the self-atom polarizabilities is presented where the diameter of a circle is proportional to the magnitude of the polarizability. The self-atom polarizabilities are always positive (actually, they are in units of $1/\beta$ and β is negative) and are an indication of the magnitude of the change in charge that will be induced at a


given atom as a result of a change in the coulomb integral (electronegativity) of that atom. The horizontal scroll bar allows the diameter of the circles to be adjusted relative to the structure. Insofar as, a charged reagent approaching an atom of a conjugated molecule induces a change in the π -electron distribution of that molecule, one might expect the self-atom polarizability to be a measure of the reactivity of the various positions within the molecule during the early transition state. The greater the polarizability of an atom, the greater the reactivity at that position.

Mutual-atom polarizability diagrams... : Mutual-atom polarizabilities denote the change in charge that will be induced at other atoms of the structure as a result of a perturbation of the coulomb integral of a given atom. The diameter of a circle is proportional to the magnitude of the polarizability; a negative polarizability is represented by an open circle and a positive polarizability is represented by a filled circle. The largest positive polarizability (filled circle) will be located on the perturbed atom and its diameter is proportional to the self-atom polarizability of that atom. A negative mutual-atom polarizability (open circle) indicates that the change in charge induced at that atom is opposite to that induced at the atom undergoing perturbation. The vertical scroll bar alters the display to show the polarizabilities as the perturbed atom is changed. The horizontal scroll bar allows the diameter of the circles to be adjusted relative to the structure.

Placing the cursor within the circles contained in any of the above diagrams will display the corresponding numeral values.

The menu entitled "**Labels**" has menu items that were previously located in the "**Results**" menu.

9. The "**Edit**" menu is now fully supported; all text and graphics can be copied to the clipboard and thereby exported any other program that will except text or PICT graphics.

10. The number of undefined atom types for which the user can assign resonance and coulomb integral parameters has been increase from three to eighteen. They are now accessed utilizing the palette tool  that activates a pop-up menu of undefined atoms.

11. In addition to simple Hückel calculations, HMO 1.4 now allows calculations to be executed using the ω -technique. The ω -technique calculations are implemented as described by Wheland and Mann [Wheland, G. W.; Mann D. E., J. Chem. Phys., **1949**, *17*, 264. See also: Streitwieser, A. J. Am. Chem. Soc., **1960**, *82*, 4123.]. The program employs the modification suggested by Ettinger that results in a more rapid convergence to a self-consistent charge distribution [Ettinger, R. Tetrahedron, **1964**, *20*, 1579]. After a structure is created and the user presses the "Calculate" tool in the palette, the dialog box shown below will appear containing the expected number of π -electrons and check boxes with which the user indicates

the desired output. Radio buttons are provided to select the calculation type. If a simple Hückel calculation is to be executed, the π -electron count is the only parameter needed. For ω -technique calculations, the user must supply the maximum number of iterations the program will perform before terminating the calculation (most calculations will reach self-consistency before 15 iterations), the criterion for a self-consistent charge distribution (usually 0.001 units), and the value of the parameter ω (omega, usually 1.4).

In addition, when executing an ω -technique calculation, the option is provided to have the off-diagonal matrix elements, corresponding to the bonded atoms, calculated from the bond orders using an iterative procedure that results in a final Hückel matrix that is self-consistent with respect to both the diagonal and off-diagonal matrix elements. The method of Boyd and Singer [Boyd, G, V.; Singer, N., Tetrahedron, **1966**, 22, 3383] is used to arrive at the off-diagonal elements that makes use of an empirical relationship between the resonance integral β_{rs} for bonded carbon atoms r and s and the bond order p_{rs} calculated for that bond: $\beta_{rs} = \beta_0 \exp(0.55p_{rs} - 0.3666)$; a new menu command, "**Resonance integral-bond order equation...**", has been added to the Parameters menu that will allow the user to change the parameters of this formula. Bond orders (p_{rs}) calculated during one cycle are used to derive the resonance integrals (β_{rs}) that are used in the next iterative cycle; the process is continued until the derived matrix elements don't change by a specified amount. In the current implementation, it was found that both the diagonal and off-diagonal elements could be optimized together within the same iterative cycle.

Boyd and Singer also describe an empirical relationship between bond length and bond order that has been incorporated into the program HMO. The relation, $R_{rs} = 1.524 - 0.194p_{rs}$ where R_{rs} is the bond length between atoms r and s and p_{rs} is the bond order, gives good predictions of the bond lengths in alternate hydrocarbons; a new menu command, "**Bond length-bond order equation...**", has been added to the Parameters menu that will allow the user to change the parameters of this equation.

A detailed description of the equations used in the ω -technique calculation is located under the Apple menu.

For ω -technique calculations, a check box can be selected that allows a separate text file to be created that contains the charge distributions and bond orders calculated during each iteration; this information is useful in situations where the calculation does not converge to a self-consistent charge distribution. Pressing the "Calculate" button then begins the calculations (see figure below).

Number of π -electrons =

Maximum iterations =

Stop when all Δq 's and Δp 's are less than:

ω =

Charges/bond orders
 Superdelocalizabilities
 Free valences
 Polarizabilities
 Save intermediate charge densities
 Bond integrals depend on bond order

Simple Hückel **ω -Technique{Wheland-Mann}**

Two parameter ω -Technique{ITPOT}

SCF {Pariser-Parr-Pople}

12. HMO also executes what has been termed an Improved Two-parameter Omega Technique calculation {ITPOT} [Mathur, S. C.; Singh, D. C.; Kumar, B.; Mitra, S., *Int. J. Quantum Chem.*, 1977, 11, 759 and Castro, E. A.; Fernández, M., *Z. Phys. Chemie, Leipzig*, 1981, 262, 83.]. In this technique, the diagonal matrix elements depend on the atomic orbital population of an atom and its neighbors and the off-diagonal elements between bonded atoms depend on the bond orders (using the same Boyd and Singer exponential relationship described above for the simple ω -technique). In the implementation used in HMO, we construct the secular determinant as described by Castro with modifications to allow calculations for structures containing heteroatoms. Since a careful analysis of the use of the default set of heteroatom coulomb and resonance integral parameters with the parameters ω and ω' has not been done, this technique should be used with caution when applied to heterocyclic systems. The calculations are very sensitive to the value of ω' . Originally, the parameters ω and ω' were assigned the values 1.4 and -0.6, respectively; in a more recent publication [Cachau, R.E.; Estiú, G.L.; Castro, E.A., *Acta Chim. Sin.* 1988, 46, 57], the values assigned were : $\omega = 1.7433$ and $\omega' = -0.495$. Preliminary indications are that these new values give a better charge distribution in heterocycles, nonalternate hydrocarbons, and ions than the original values. A

detailed description of the equations used in the ITPOT calculations is located under the Apple menu.

13. Polarographic half-wave reduction potentials are calculated as described by Fry and Fox [Fry, A.J.; Fox, P.C., Tetrahedron, 1986, 42, 5266]. The empirical equations described in the above reference are used for calculating the reduction potentials when doing a Hückel or ω -technique calculation. For ITPOT calculations, a linear equation [$E_{1/2} = 2.82 \times m\langle\text{lumo}\rangle - 0.0279$, $R = .98$] was derived using a subset of the Fry and Fox data with $\omega = 1.7433$ and $\omega' = -0.495$.