

132. Computer-Drawn Molecular Orbitals: An Aid for the Users of MO-programs

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Summary. A computer program is described, which generates a simplified pictorial representation of computed molecular orbitals. As examples, the highest occupied MO's of the two C_s -rotamers of the cyclopropylcarbinylcation ($C_4H_7^+$), of pyridine and of barrelene (bicyclo[2.2.2]octatriene) are given.

Introduction

The use of approximate quantum chemical procedures by chemists or spectroscopists has become widely popular. However, all users are aware of the considerable effort necessary to extract the wanted information from the rather formidable tables of numbers in the standard computer output. This is particularly true for the molecular orbitals since these are usually given in terms of unhybridized basis functions. Hence it is in general impossible to gain quickly insight into the symmetry, nodal properties and phase relationships of these molecular orbitals.

We have therefore written a computer program which draws the MO's of molecular systems composed of first and second row elements. This routine might prove to be particularly helpful, for instance, for discussions involving the *Woodward-Hoffmann* rules [1] or for the interpretation of photoelectron spectra on the basis of *Koopmans'* theorem [2].

Program description

For a given molecule the input to our program consists essentially of:

1. the cartesian coordinates of the atoms,
2. the coefficients of the basis orbitals in the LCAO-expansion for each MO to be plotted. These can be obtained by any of the currently available semiempirical methods such as the extended *Hückel* method [3], CNDO/2 [4], MINDO/2 [5], etc.,
3. some transformation matrix which allows one to rotate the whole molecular framework until a convenient view is obtained.

The main objective is to obtain the information concerning phase, symmetry, etc. in a reasonable amount of computing and plotting time on even a rather small computer. This forbids the use of the basis function (*e.g.* *Slater* type or *Hartree-Fock* functions) for the representation of the hybrids and suggests a different simplified approach.

Consider a particular MO of a system, c_s , c_x , c_y , c_z being the coefficients of the basis functions ($2s$ -, $2p_x$ -, $2p_y$ - and $2p_z$ -AO's) at a second-row nucleus M . Since p-AO's transform like vectors the latter three coefficients define the three vectors \mathbf{c}_x , \mathbf{c}_y , \mathbf{c}_z and these in turn the vector \mathbf{c}_p of maximum p-character with

$$\mathbf{c}_p = \mathbf{c}_x + \mathbf{c}_y + \mathbf{c}_z; \quad |\mathbf{c}_p| = \sqrt{c_x^2 + c_y^2 + c_z^2}. \quad (1)$$

We distinguish arbitrarily between two cases:

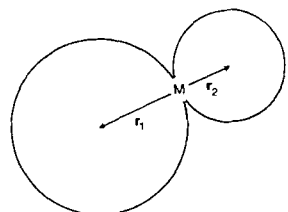
$$\text{a) } |c_s| \geq |c_p|.$$

In this case the hybrid is primarily of s-character and will therefore be represented by a single sphere containing M . The center of the sphere (radius r) is shifted from the position of M by a vector l depending on the p-character of the hybrid and defined as follows:

$$\begin{aligned} l &= \frac{r}{|c_s|} c_p \\ r &= \sqrt{c_s^2 + |c_p|^2} \end{aligned} \quad \text{b) } |c_s| < |c_p|$$

(2)

In this case the hybrid is mainly of p-character and will therefore be represented by two spheres tangent in M . The positions of their centers relative to M are defined by:

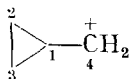
$$\begin{aligned} r_1 &= \frac{1}{\sqrt{2}} \left(1 + \frac{c_s}{|c_p|} \right) c_p \\ r_2 &= -\frac{1}{\sqrt{2}} \left(1 - \frac{c_s}{|c_p|} \right) c_p \end{aligned}$$

(3)

It is easily seen that in both cases the total area of the circle(s) – obtained after projecting the sphere(s) – is proportional to the total electron density around M , *i.e.* $(c_s^2 + c_x^2 + c_y^2 + c_z^2)$. In particular the cases a) and b) become identical for $|c_s| = |c_p|$ and only one sphere of radius $r = \sqrt{2} |c_p|$ passing through M will be drawn. This seems rather unrealistic if compared with the commonly given picture for a 'pure' sp-hybrid. However, the latter is also only an arbitrary representation of the angular dependence of $1/\sqrt{2} (s + p)$ since for hybrids a product separation between the angular and the radial parts of *e.g.* Slater type functions cannot be achieved. On the other hand, spectroscopists and chemists usually deal only with the few highest occupied and lowest virtual MO's. In this case $|c_p| \gg |c_s|$, and the picture obtained according to the above recipe will therefore be quite familiar.

The orbital sign problem can be handled by the program in two ways, either by using different colours for plus and minus lobes or by drawing the circles in full or dotted lines. For obvious reasons we have chosen the latter option for the examples given below.

Examples

As a first example we illustrate the well known experimental fact that carbonium ions are significantly stabilized by an adjacent cyclopropyl ring, provided that the empty p-AO can achieve an orientation parallel to the plane of the ring [6]. This



effect can be nicely demonstrated by considering the two possible rotamers of C_s -symmetry (I and II) of cyclopropylcarbinyl-cation $C_4H_7^+$, for which we have performed MINDO/2-calculations [5] and plotted the two highest occupied MO's, which are symmetric (S) and antisymmetric (A) with respect to the plane of symmetry (Fig. 1).

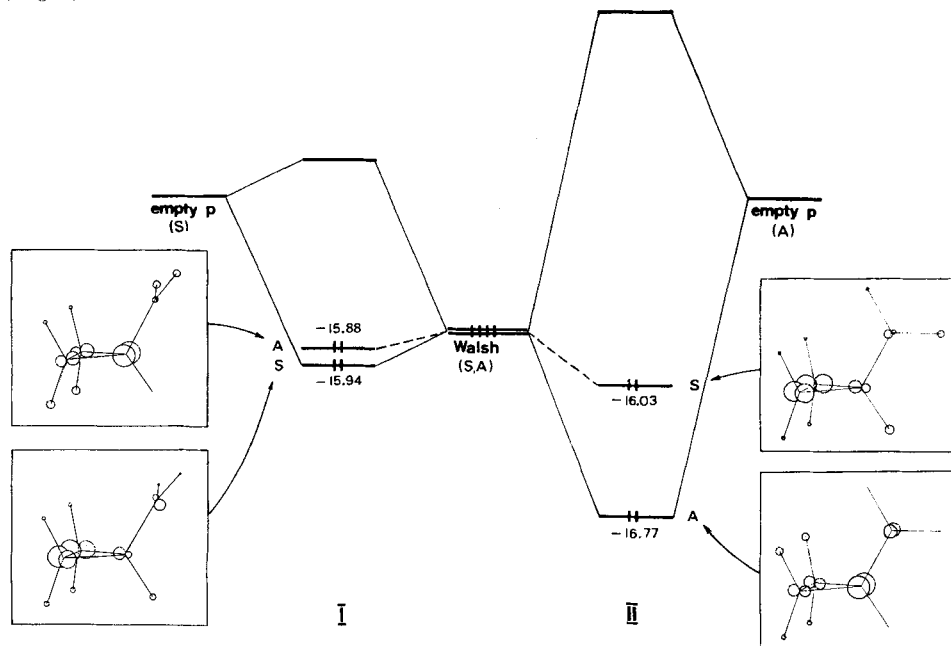


Fig. 1. Correlation diagram for the interaction of the p-orbital of a CH_2 -group with the Walsh orbitals of cyclopropane

Given are the computer drawn MO's and their orbital energies (in eV; obtained by MINDO/2 calculations)

As expected, these two MO's are for both rotamers essentially localized in the three-membered ring and therefore of *Walsh* type [7]. In I the slight lowering of the S-orbital (-0.06 eV) relative to the A-orbital is due to a weak coupling between the empty p-AO at C(4) and the symmetric *Walsh* MO. In II, however, the empty p-AO interacts with the antisymmetric *Walsh* MO having a large coefficient at C(1). This π -type interaction is significant and results in a lowering of the A-orbital (-0.8 eV) relative to the S-orbital.

Such reasoning might be misleading in many cases, particularly when dealing with charged species, since the relative stability of such conformers depends on the total molecular energy which, in the *Hartree-Fock* picture, is composed of orbital energies and repulsive contributions (interelectron- and internuclear repulsion) [8]. Indeed some 'repulsive dominant' stabilization phenomena have been found recently [9] (for the interesting case $n-C_3H_7^+$ vs. $i-C_3H_7^+$, see [10]); in these cases simple orbital arguments are in principle not applicable. In our case, however, inspection of the MINDO/2 total molecular energies of I and II confirm the conclusions drawn from the orbital correlation diagram (Fig. 1) since we predict II to be more stable than I by 10.2 kcal/mole, in good agreement with the observed rotational barrier in dimethylcyclopropylcarbinyl-cation (13.7 kcal/mole) [11]. (The calculated value refers, of course, to the gas phase, like all quantitative

conclusions drawn from MO theory.) Energy partitioning indicates that the barrier is 'attractive dominant' in nature.

As a further example we have drawn that occupied MO of pyridine belonging to the representation A_1 , which is usually thought of as being the 'lone-pair' n-orbital. Fig. 2 shows that it is fairly well distributed over the whole nuclear framework. (Using the numerical values of the coefficients we find that the 'lone-pair' electrons reside only to 53% on the nitrogen atom.) This is, of course, in agreement with con-

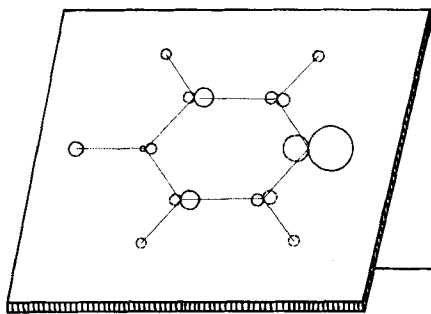


Fig. 2. Pictorial representation of the highest occupied A_1 -orbital in pyridine (commonly referred to as being the 'lone-pair' orbital)

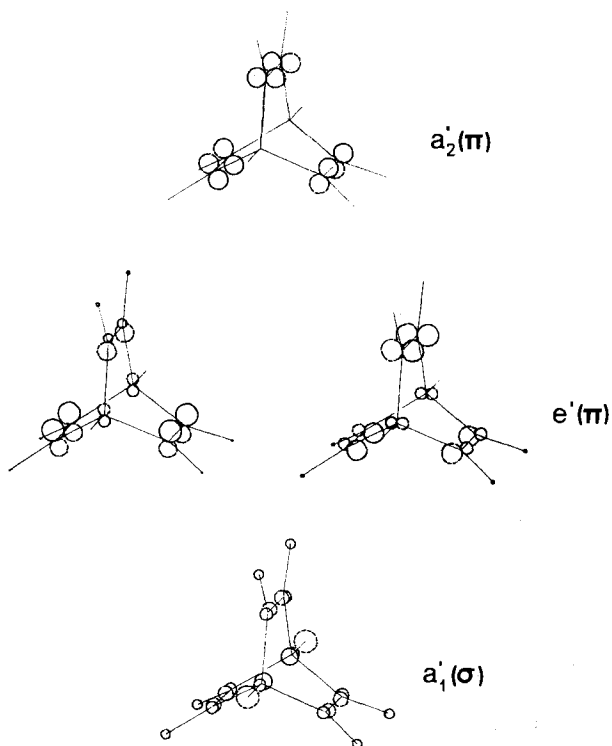


Fig. 3. The four highest occupied MO's of barrelene (see also [15])

clusions reached earlier on the basis of extended *Hückel* calculations [12] and from photoelectron spectroscopic studies on other nitrogen compounds [13]. Furthermore the ESR. spectrum of $C_5H_5N^+$ indicates that the unpaired electron moves in a σ -type MO, the spin density being about equal in magnitude at the nitrogen atom and in the rest of the ring [14].

The third example shows the four top occupied MO's of barrelene (Fig. 3), the photoelectron spectrum of which has been recorded recently in our laboratory [15]. For interpreting the spectrum a pictorial representation of these MO's using MINDO/2 wave functions has proved to be of great help, particularly for the discussion of the vibrational fine-structure patterns of the first band.

This example reveals a difficulty which one encounters in plotting degenerate MO's. Most diagonalization routines employed in quantum chemistry generate the real eigenvectors associated with a degenerate eigenvalue in an arbitrary orientation, which often yields rather obscure and useless pictorial representations. A way round this difficulty is to subject each set of degenerate MO's to be plotted to a (physically irrelevant) orthogonal transformation, employing, for instance, the condition that the new components shall be symmetric or antisymmetric with respect to some secondary symmetry element of the particular symmetry group of the molecule.

The plotting program will be soon ready for distribution. A listing can be obtained on request.

This work has been performed on a PDP-9 computer connected to a 565-CALCOMP plotter.

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