

# A simple method to display molecular orbitals with computer graphics

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A computer program named *LOBE* was developed to draw molecular orbitals as lobes on a graphic display. With this program, any molecular orbital of large molecules can be displayed quickly. This program is suitable not only for general-purpose computers but also for microcomputers. A sample application is used to illustrate the program.

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Molecular orbital theory is a powerful tool to predict chemical phenomena and the physical properties of molecules.<sup>1</sup> For example, it is possible to predict regio- and stereo-selectivity in chemical reactions by examining the distribution of frontier orbitals.<sup>2</sup> So the display of molecular orbitals is of interest. To generate three-dimensional (3D) molecular orbital plots, wire-frame representations<sup>3</sup> have been widely used. Shaded versions,<sup>4</sup> by which the shape of molecular orbitals can be understood more readily, have recently been used as well. These are accurate ways to represent the equivalued surface of a molecular orbital. However, it is time-consuming to display them with computer graphics, especially for large molecules. Another, more qualitative representation of molecular orbitals, called lobe representation, is used in many textbooks and articles on quantum chemistry.<sup>5</sup> The contributions to a molecular orbital from atomic orbitals are summed for each atom and independently drawn as lobes on it, generally by hand.

In this paper, we describe a method to display lobes with computer graphics. With this method, molecular orbitals can be drawn much faster than either wire-frame or shaded representations. The program developed here can be run not only on general-purpose computers but also on microcomputers. Although the lobe representation is qualitative, it is accurate enough to enable recognition of the distribution or symmetry of the molecular orbital.

## METHODS

In the program reported here, contributions to a molecular orbital from atomic orbitals are summed for each atom and independently sketched as lobes on it, in the usual way. Only *s*- and *p*-type atomic orbitals are considered,

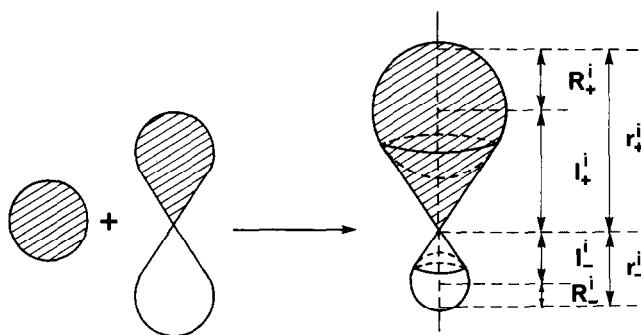


Figure 1. Construction of an *sp*-type lobe

because it is difficult to display a summation of atomic orbitals with a higher angular quantum number such as a *d*-type lobe. Only outer shells are dealt with. Therefore, this method is applicable to molecular orbitals composed of *s*- and *p*-type atomic orbitals only.

To draw the *sp*-type lobe, first, three *p*-type atomic orbitals ( $p_x$ ,  $p_y$  and  $p_z$ ) on each atom are summed as vectors. The *p*-type atomic orbital composed in this way will be called  $p_c$  here. Second, each  $p_c$  orbital is summed with the *s*-type atomic orbital that belongs to the same atom. In this step, the shape of the lobe is decided by the method shown in Figure 1. The lobe is constructed from two spheres, the radii of which are  $R_+^i$  and  $R_-^i$ , respectively, and two cones, both with vertical angles of  $60^\circ$ . This value was decided with reference to lobes shown in textbooks on quantum chemistry; it is not based on any explicitly defined physical value. The superscript *i* indicates that the values are related to the *i*th atom. The shaded part is the plus phase, and the other part is the minus phase. The length of the plus phase along the axis of the  $p_c$  orbital is  $r_+^i$ , and that of the minus phase is  $r_-^i$ . These are the solutions of equations 1 and 2 on the axis of the  $p_c$  orbital, respectively. In these equations, the *d* value is a constant, and the value of 0.05 was taken in the same way as that taken for the decision of the vertical angles of cones.  $\chi_s^i$  and  $C_{p_c}^i$  are the *s*-type atomic orbital and the  $p_c$  orbital, respectively, and belong to the outer shell of the *i*th atom. The *n* value in equations 4 and 5 is the principal quantum number of the outer shell of the *i*th atom.  $N_s^i$  and  $N_p^i$  are the normalizing factors.  $\alpha_s^i$  and  $\alpha_p^i$  are the orbital exponents.  $\Theta$  is  $0^\circ$  or  $180^\circ$  on the axis of the  $p_c$  orbital.  $C_s^i$  and  $C_{p_x}^i$ ,  $C_{p_y}^i$  and  $C_{p_z}^i$  in equation 3 are the molecular orbital coefficients for the *i*th atom.

$$C_s^i \chi_s^i + C_{pc}^i \chi_{pc}^i = d \quad (1)$$

$$C_s^i \chi_s^i + C_{pc}^i \chi_{pc}^i = -d \quad (2)$$

$$C_{pc}^i = [(C_{px}^i)^2 + (C_{py}^i)^2 + (C_{pz}^i)^2]^{1/2} \quad (3)$$

$$\chi_s^i = N_s^i r^{n-1} \exp(-\alpha_s^i r) \quad (4)$$

$$\chi_{pc}^i = N_p^i r^{n-1} \cos \theta \exp(-\alpha_p^i r) \quad (5)$$

These equations are solved numerically.

$R_+^i$  and  $R_-^i$  in Figure 1, the solutions of equations 6 and 7, are  $1/3 r_+^i$  and  $1/3 r_-^i$ , respectively.

$$R_+^i/(r_+^i - R_+^i) = \sin 30^\circ \quad (6)$$

$$R_-^i/(r_-^i - R_-^i) = \sin 30^\circ \quad (7)$$

Then  $l_+^i$  and  $l_-^i$ , which are the distances from the center of the  $i$ th atom to the center of one sphere and the center of the other sphere, respectively, are  $2/3 r_+^i$  and  $2/3 r_-^i$ , and the Cartesian coordinates of the centers of the sphere are

$$[(C_{px}^i/C_{pc}^i)l_+^i + x^i, (C_{py}^i/C_{pc}^i)l_+^i + y^i, (C_{pz}^i/C_{pc}^i)l_+^i + z^i]$$

for the plus phase, and

$$[-(C_{px}^i/C_{pc}^i)l_-^i + x^i, -(C_{py}^i/C_{pc}^i)l_-^i + y^i, -(C_{pz}^i/C_{pc}^i)l_-^i + z^i]$$

for the minus phase, where  $[x^i, y^i, z^i]$  are the Cartesian coordinates of the center of the  $i$ th atom. If only one or the other of equations 1 and 2 has solutions, the lobe is of  $s$ -type and is drawn as a sphere, the radius of which is  $(r + r')/2$ ;  $r$  and  $r'$  are the solutions, and the center of the sphere coincides with the center of the atom. If neither equation 1 nor 2 has solutions, the lobe is not drawn. For a hydrogen or helium atom, the lobe is drawn as a sphere, the radius of which is the solution of equation 8, where  $\chi_{1s}$  is the  $1s$ -atomic orbital of the hydrogen or helium atom (see equation 4; in this case,  $n = 1$ ) and  $C_{1s}$  is the molecular orbital coefficient for the atom. The  $d$  value in this equation is the same as that in equations 1 and 2.

$$|C_{1s} \chi_{1s}| = d \quad (8)$$

The sphere is shaded if  $C_{1s}$  is plus; otherwise, it is not shaded. The center of the sphere coincides with that of the atom.

After the shapes of lobes are decided for all atoms, they are displayed with bonds by hidden-line and hidden-surface treatment. In this step, the points of intersection between lobes and bonds are obtained analytically. In the color graphics, the plus and minus phases of lobes are colored red and green, respectively.

## GRAPHIC SYSTEM AND PROGRAMS

Our graphic system is an N6965 color display with a NEC ACOS430/20 host computer. The LOBE program is written in FORTRAN. The program can be executed even on microcomputers such as the NEC PC-9801.

## RESULTS AND DISCUSSION

The molecular orbitals of the dianion of protoporphyrin IX were used to illustrate the LOBE program. Chelation of  $\text{Fe}^{2+}$  to the dianion gives heme, the prosthetic group of proteins such as myoglobin, hemoglobin, catalase, peroxidase, and cytochromes  $c$  and  $P450$ , which has important biochemical functions.

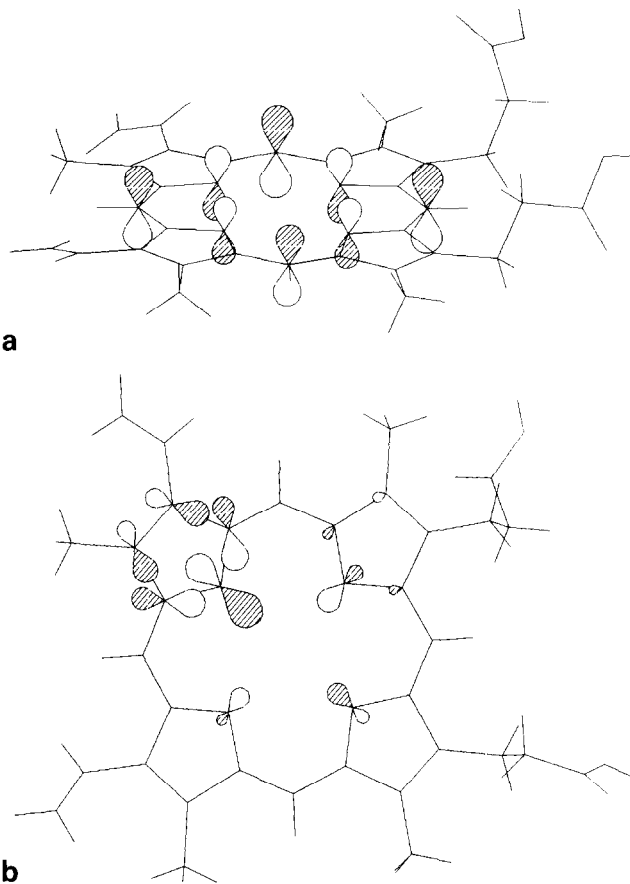


Figure 2. Molecular orbitals of protoporphyrin IX dianion: (a) HOMO, (b) the highest lone-pair orbital

Cartesian coordinates of protoporphyrin IX dimethyl ester were obtained from the Cambridge Crystal Database.<sup>6</sup> Hydrogen atoms were substituted for the methyl groups in the ester moieties, and the two hydrogen atoms that were bonded to nitrogen atoms were removed. The Cartesian coordinates of one hydrogen atom belonging to a methyl group were lacking; they were obtained by use of the standard geometry of methyl groups. In this way, the Cartesian coordinates of the dianion of protoporphyrin IX were obtained, and molecular orbitals were calculated with the MNDO method.<sup>7</sup>

Figure 2 shows two of the molecular orbitals of the protoporphyrin IX dianion that are probably responsible<sup>8</sup> for interactions with atomic orbitals of  $\text{Fe}^{2+}$ . Figures 2(a) and 2(b) show HOMO and the highest lone-pair orbital, respectively.

With the LOBE program, the molecular orbitals of the protoporphyrin IX dianion could be displayed very quickly, and the interactions between them and the atomic orbitals of  $\text{Fe}^{2+}$  could be predicted qualitatively. Although the lobe representation is qualitative, it is adequate for the recognition of the distribution or symmetry of a molecular orbital. It is time-consuming even with a general-purpose computer to display the 3D equivalued surface of a molecular orbital for such a large molecule. This is a drawback of wire-frame and shaded representations, especially when molecular orbital theory is applied to drug design, because drugs are generally large molecules. The LOBE program is probably suitable for integration into drug design systems such as the Advanced Computer-Aided Chemistry System (ACACS),<sup>9</sup> which was jointly developed by

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