Molecular Orbital Densities: Pictorial Studies

Comparisons of the hydrogen, lithium, boron, carbon, nitrogen, oxygen, and fluorine molecules.

Arnold C. Wahl

For many years physicists and chemists have been attempting to construct an adequate model of molecular structure. The major difficulty in constructing such a model within a rigorous mathematical framework arises from the intractable multidimensional differential equations which quantum mechanics demands as the proper description of such systems of electrons and nuclei.

One of the most fruitful approaches to this problem was introduced in 1932 by R. S. Mulliken and F. Hurd. In a now classic paper (*1*), they developed the orbital theory or "shell model" that has proven so useful in molecular spectroscopy and as a working intuitive set of symbols for quantum chemists. The essence of the theory is that electrons occupy distinct orbitals which may be characterized by a set of space and spin molecular quantum numbers and from which the total molecule may be constructed.

Until recently, however, the quantitative accuracy of this orbital model was poor, and it found its greatest use as an interpretive tool. Today, because of the rapid development of large electronic computers and the concurrent sophistication in their use, it has become possible to perform the tremendous amount of algebra and arithmetic associated with the rigorous mathematical calculation of the exact properties of this shell model for diatomic molecules (*2–5*). An important outcome of these calculations is that the model is now documented and its usefulness is being demonstrated (*6–9*). However, if the advances and refinements of this model can be described only in complex mathematical language or in terms of vast undigestable (and often misleading) numerical tables, they will have limited value.

Further, it has been as a general, qualitative symbol that such models of molecular structure have proven very useful in providing new concepts for both experimental and theoretical investigators.

The above considerations motivated the present computational task of displaying directly these calculated molecular orbital and total molecular densities. I also hope that this effort provides an example of the presentation of computer computations in an obvious, compact, and provocative way, making a part of the rich rewards of these calculations more readily available to a wider and therefore potentially more fertile audience.

Review of Theory

According to molecular orbital theory (*1*), the electronic structure of, for example, the fluorine molecule (F_2) is written (*2*)

$$1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 2\sigma_u^2\, 1\pi_u^4\, 3\sigma_g^2\, 1\pi_g^4 : {}^1\Sigma_g^+$$

This indicates that there are two electrons in the $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, and $3\sigma_g$ shells and four electrons in the $1\pi_u$ and $1\pi_g$ shells; ${}^1\Sigma_g^+$ is the spectroscopic notation for the ground state of the F_2 molecule. The corresponding electron configurations of the molecules studied in this work are given in Table 1.

Mathematically, the total N-electron wave function is put forth as an antisymmetrical product of molecular spin orbitals (*2, 5*).

$$\chi_\kappa^\mu = \varphi_{i(\kappa)}{}^\mu\, \eta_\kappa{}^\mu, \qquad (1)$$

where μ stands for the space and spin coordinates of the μth electron and κ and i label the different molecular spin orbitals and molecular orbitals, respectively. In the following, the superscript μ and subscript κ are dropped in order to simplify the presentation.

In order to find the molecular orbitals, the total energy of the molecule would be varied with respect to the form of the molecular orbitals and the minimum found. However, because of current mathematical obstacles, the most convenient method of finding the molecular orbitals φ_i is to expand them in terms of a set of suitable expansion functions χ_p,

$$\varphi_i = \sum_p C_{ip}\, \chi_p \qquad (2)$$

where the C_{ip}'s are determined by the variational procedure, customarily through the iterative self-consistent field process (*2, 4, 5*).

In practice a very close approximation to the molecular orbitals can be obtained in this way. Calculations of this type using analysis and computer programs developed recently (*2, 3*) have resulted in the determination of the molecular orbitals for a large number of diatomic molecules in the form of Eq. 2. These functions (*2, 7*), which are very close to the Hartree-Fock (that is, the molecular orbitals demanded by theory) result, were used in the pictorial calculations presented here.

Densities and Contours

At this point, in order to clarify the diagrams of the shell model, it is convenient to introduce two new indices, λ and α, which indicate, respectively, the symmetry species and subspecies of the molecular orbitals φ_i. The electronic density $\rho_{i\lambda}$ associated with the $i\lambda$th molecular shell at a point $\mathbf{r}$ in space is defined by

$$\rho_{i\lambda}(\mathbf{r}) = e^- N_{i\lambda} d_\lambda^{-1} \sum_\alpha \varphi_{i\lambda\alpha}(\mathbf{r})\, \varphi^*_{i\lambda\alpha}(\mathbf{r}) \qquad (3)$$

where we have now grouped the molecular orbitals $\varphi_{i\lambda\alpha}$ according to their symmetry species λ and subspecies α and have defined the density of shell $i\lambda$ which contains $N_{i\lambda}$ electrons in terms of the sum over the modulus squared of the d_λ degenerate molecular orbitals making up the shell. The total electron density $\rho(\mathbf{r})$ of the molecule is then given by

$$\rho(\mathbf{r}) = \sum_\lambda \sum_i \rho_{i\lambda}(\mathbf{r}) \qquad (4)$$

and is thus the sum of the densities of all shells making up the molecule.

The author was formerly a member of the Chemistry Division, Argonne National Laboratory. He is currently professor of chemistry, University of Wisconsin, Madison 53715.

Table 1. Electron configuration of molecules. Superscript indicates the number of electrons, $N_{i\lambda}$, occupying molecular shell $i\lambda$. Number of diagram (see Figs. 1 to 41) is in parentheses to the right of each symbol. For the π shells, which consist of two degenerate molecular orbitals, a molecular orbital, containing half the electrons in the π shell, has been plotted.

Total molecular density	Molecular shells and index to contour diagrams																Spectroscopic designation
	$1\sigma_g$		$1\bar{\sigma}_u$		$2\sigma_g$		$2\bar{\sigma}_u$		$1\pi_u$		$3\sigma_g$		$1\pi_g$		$3\sigma_u$		
H_2 (1)	$1\sigma_g^2$	(2)															$^1\Sigma_g^+$
He_2	$1\sigma_g^2$		$1\bar{\sigma}_u^2$														$^1\Sigma_g^+$
Li_2 (3)	$1\sigma_g^2$	(4)	$1\bar{\sigma}_u^2$	(5)	$2\sigma_g^2$	(6)											$^1\Sigma_g^+$
Be_2	$1\sigma_g^2$		$1\bar{\sigma}_u^2$		$2\sigma_g^2$		$2\sigma_u^2$										$^1\Sigma_g^+$
B_2 (7)	$1\sigma_g^2$	(8)	$1\sigma_u^2$	(9)	$2\sigma_g^2$	(10)	$2\sigma_u$	(11)	$1\pi_u^2$	(12)							$^3\Sigma_g^-$
C_2 (13)	$1\sigma_g^2$	(14)	$1\sigma_u^2$	(15)	$2\sigma_g^2$	(16)	$2\sigma_u^2$	(17)	$1\pi_u^4$	(18)							$^1\Sigma_g^+$
N_2 (19)	$1\sigma_g^2$	(20)	$1\bar{\sigma}_u^2$	(21)	$2\sigma_g^2$	(22)	$2\sigma_u^2$	(23)	$1\pi_u^4$	(24)	$3\sigma_g^2$	(25)					$^1\Sigma_g^+$
O_2 (26)	$1\sigma_g^2$	(27)	$1\sigma_u^2$	(28)	$2\sigma_g^2$	(29)	$2\sigma_u^2$	(30)	$1\pi_u^4$	(31)	$3\sigma_g^2$	(32)	$1\pi_g^2$	(33)			$^3\Sigma_g^-$
F_2 (34)	$1\sigma_g^2$	(35)	$1\bar{\sigma}_u^2$	(36)	$2\sigma_g^2$	(37)	$2\sigma_u^2$	(38)	$1\pi_u^4$	(39)	$3\sigma_g^2$	(40)	$1\pi_g^4$	(41)			$^1\Sigma_g^+$
Ne_2	$1\sigma_g^2$		$1\bar{\sigma}_u^2$		$2\sigma_g^2$		$2\sigma_u^2$		$1\pi_u^4$		$3\sigma_g^2$		$1\pi_g^4$		$3\sigma_u^2$		$^1\Sigma_g^+$

The density associated with one of the d_λ degenerate molecular orbitals $\varphi_{i\lambda\alpha}$ making up shell $i\lambda$ is

$$\rho_{i\lambda\alpha}(\mathbf{r}) = \rho_{i\lambda}(\mathbf{r})/d_\lambda \qquad (5)$$

which is just the shell density divided by the number of degenerate molecular orbitals making up the shell. In the diagrams presented in this article it is the total density (Eq. 4) and the orbital density (Eq. 5) which have been plotted. [For σ symmetry, $d_\lambda = 1$, and thus the orbital density equals the shell density; for π symmetry in diatomic molecules $d_\lambda = 2$, and the orbital density equals ½ the shell density. The molecular shells and their occupation $N_{i\lambda}$ are given in Table 1 for the molecules studied. The only molecular symmetries occurring in this work are σ_g, σ_u, π_u, and π_g (*1*).]

In what follows, the symmetry indices λ and α of the orbital density $\rho_{i\lambda\alpha}(\mathbf{r})$ will be suppressed, since they are unnecessary for the description of the contour drawing process.

An orbital contour line indicating a density C in the XZ (ρ and ρ_i for diatomic molecules are cylindrically symmetric about the z-axis and plots in any plane containing this axis convey complete density information) plane may be defined by the equation,

$$\rho_i(x, z) = C$$

and its path by the relation,

$$\frac{d\rho_i}{dx}\Delta x + \frac{d\rho_i}{dz}\Delta z = 0$$

which gives the direction of the tangent to the contour at any point on it to be

$$\frac{\Delta x}{\Delta z} = -\frac{d\rho_i/dz}{d\rho_i/dx} \qquad (6)$$

A step $\Delta s = (\Delta x^2 + \Delta z^2)^{\frac{1}{2}}$ is taken along this tangent and a density found such that

$$\rho_i'(x + \Delta x, z + \Delta z) = C + \Delta\rho_i \qquad (7)$$

A correction is applied perpendicular to the initial tangent along the new line

$$\frac{\Delta z'}{\Delta x'} = +\frac{d\rho_i/dx}{d\rho_i/dz}$$

at a distance

$$\Delta z' = \frac{\Delta\rho}{\left(\dfrac{d\rho_i'}{dz'} + \dfrac{d\rho_i'\, d\rho_i/dx}{dx'\, d\rho_i/dz}\right)} \qquad (8)$$

This correction (Eq. 8) is continued until $\Delta\rho$ falls within a small pre-set threshold. This hunt process (Eqs. 6 to 8) is continued until the entire contour is traced out. Analogous equations result for the total molecular density or for any linear combination of molecular orbital densities.

Computer Program

When the molecular orbitals are expanded in terms of a linear combination of symmetry expansion functions

$$\varphi_{i\lambda\alpha} = \sum_p C_{ip\lambda}\chi_{p\lambda\alpha},$$

where for convenience the expansion functions possess the same symmetry as the molecular orbital (*2*), then Eqs. 4 and 5 become

$$\rho(\mathbf{r}) = e^- \sum_\lambda \sum_i N_{i\lambda} \left| \sum_p C_{ip\lambda}\chi_{p\lambda\alpha}(\mathbf{r}) \right|^2 \qquad (9)$$

$$\rho_{i\lambda\alpha}(\mathbf{r}) = e^- N_{i\lambda} d_\lambda^{-1} \left| \sum_p C_{ip\lambda}\chi_{p\lambda\alpha}(\mathbf{r}) \right|^2 \qquad (10)$$

In going from Eqs. 4 and 5 the summation over α has been eliminated, since it yields d_λ identical contributions.

Again dropping symmetry indices, Eq. 6 becomes

$$\frac{\Delta x}{\Delta z} = \frac{\left[\sum_{pq} C_{ip}C_{iq}\left(\chi_p\dfrac{d\chi_q}{dz} + \chi_q\dfrac{d\chi_p}{dz}\right)\right]}{\left[\sum_{pq} C_{ip}C_{iq}\left(\chi_p\dfrac{d\chi_q}{dx} + \chi_q\dfrac{d\chi_p}{dx}\right)\right]} \qquad (11)$$

In this study the expansion functions χ_p used were the two center symmetry Slater type basis functions employed in self-consistent field calculations described recently (*2*). The derivatives of these functions can be evaluated in a straightforward fashion.

I constructed general automatic programs for the CDC 3600 computer with an on-line DD 80 plotter (at Argonne National Laboratory) which automatically hunted and plotted a given set of contour values for a single or linear combination of molecular orbitals φ_i in the expansion form for either homonuclear or heteronuclear diatomic molecules. With the use of Eq. 10 a contour value was found, and a contour line was hunted out by proceeding along the tangent (Eq. 11) a small increment and interating perpendicular to the tangent (that is, along the new line $\Delta x'/\Delta y' = -\Delta y/\Delta x$) until the contour value was relocated with 1 percent. By the repetition of this process the entire contour was traced out. Straight line segments were

Figs. 1–41 (next 3 pages). The shell models of molecules. Diagrams 1–41 are contour diagrams of the electron densities characteristic of the shell models of the molecules H_2, Li_2, B_2, C_2, N_2, O_2, and F_2. Both the total molecular density and the constituent shell densities are displayed at the experimental internuclear distance of each molecule. (He_2, Be_2, and Ne_2, which are members of this homonuclear series, are not bound in their ground state and therefore are not displayed.)

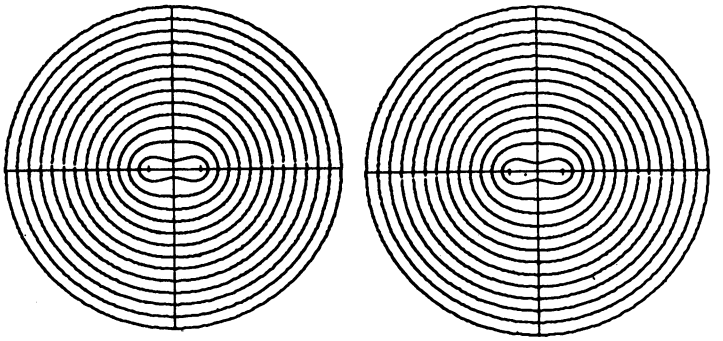


Fig. 1 (left). Hydrogen Molecule Total Electron Density Contours. Fig. 2 (right). Hydrogen Molecule 1 Sigma G Orbital Contours.

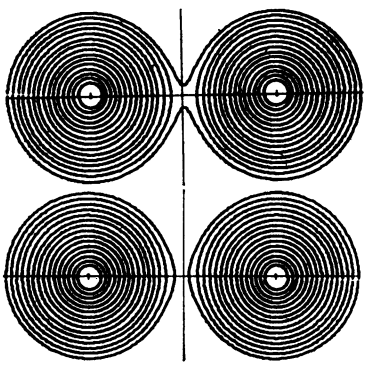


Fig. 4 (left). Lithium Molecule 1 Sigma G Orbital Contours.

Fig. 5 (left). Lithium Molecule 1 Sigma U Orbital Contours.

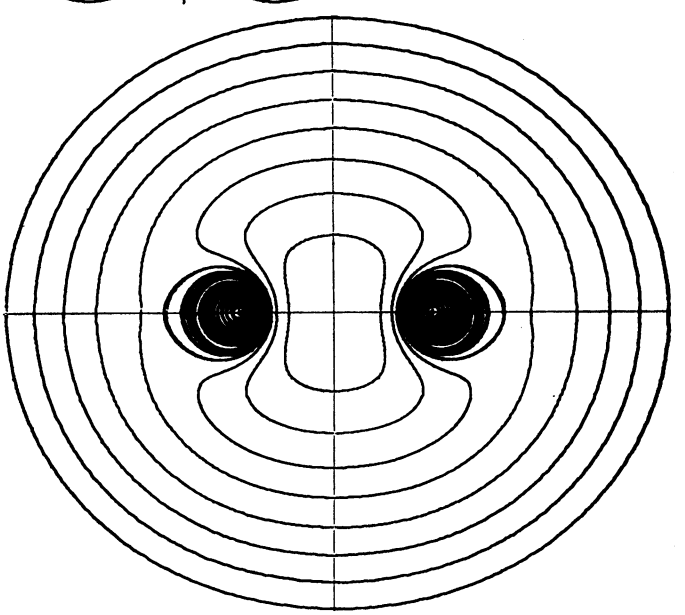


Fig. 6. Lithium Molecule 2 Sigma G Orbital Contours.

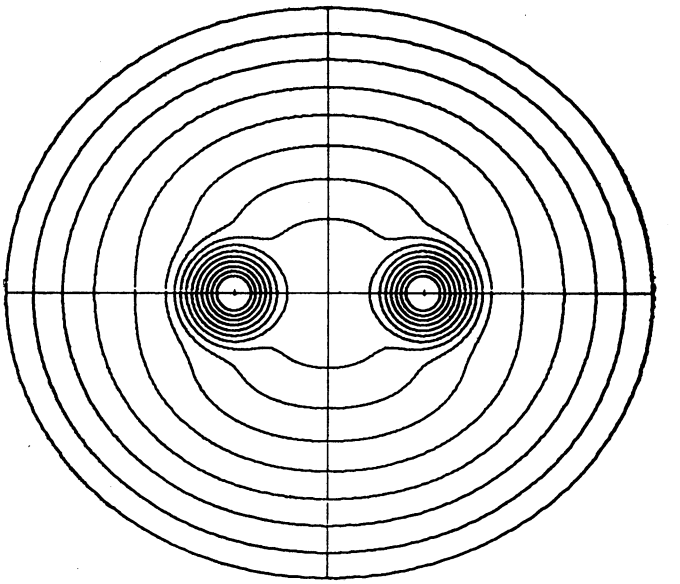


Fig. 3. Lithium Molecule Total Electron Density Contours.

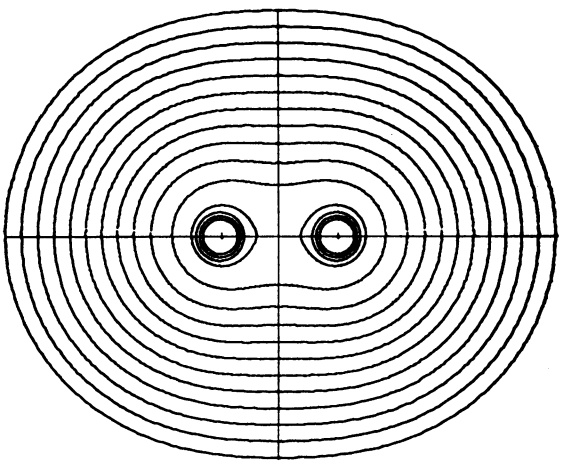


Fig. 7. Boron Molecule Total Electron Density Contours.

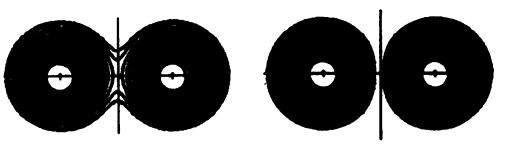
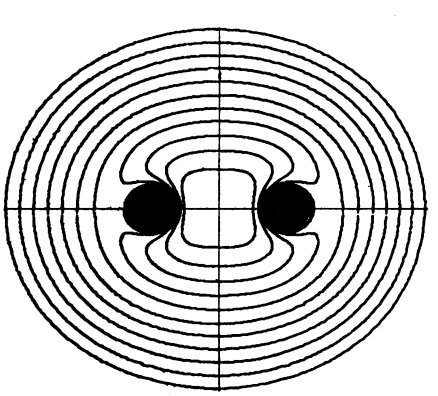
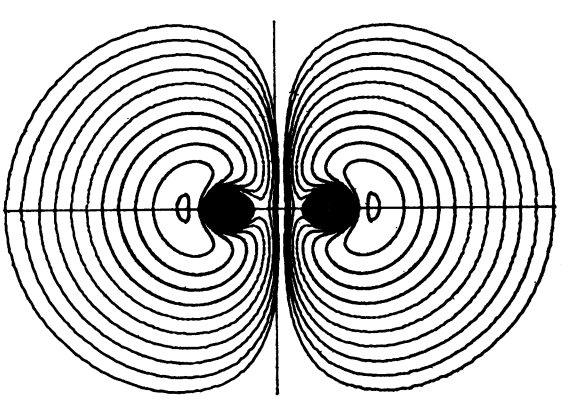


Fig. 8 (left). Boron Molecule 1 Sigma G Orbital Contours. Fig. 9 (right). Boron Molecule 1 Sigma U Orbital Contours.





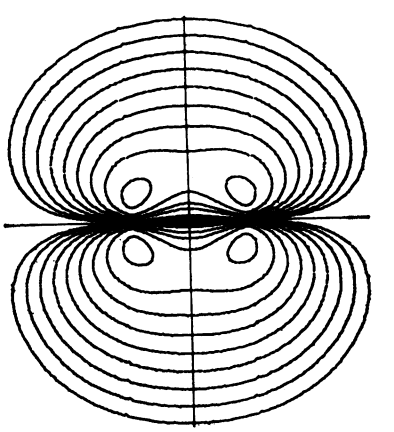


Fig. 10 (left). Boron Molecule 2 Sigma G Orbital Contours. Fig. 11 (center). Boron Molecule 2 Sigma U Orbital Contours. Fig. 12 (right). Boron Molecule 1 P1 U Orbital Contours.

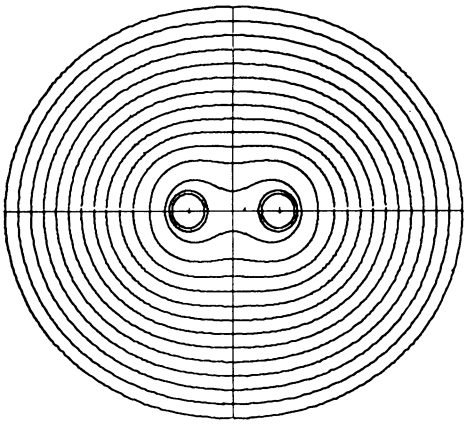


Fig. 13. Carbon Molecule Total Electron Density Contours.

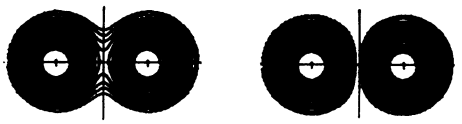


Fig. 14 (left). Carbon 1 Sigma G Orbital Contours. Fig. 15 (right). Carbon Molecule 1 Sigma U Orbital Contours.

Fig. 20 (left). Nitrogen Molecule 1 Sigma G Orbital Contours. Fig. 21 (right). Nitrogen 1 Sigma U Orbital Contours.

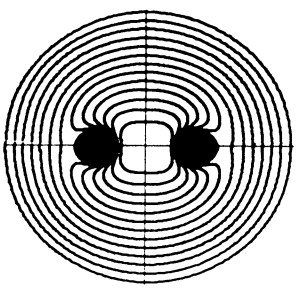


Fig. 22. Nitrogen 2 Sigma G Orbital Contours.

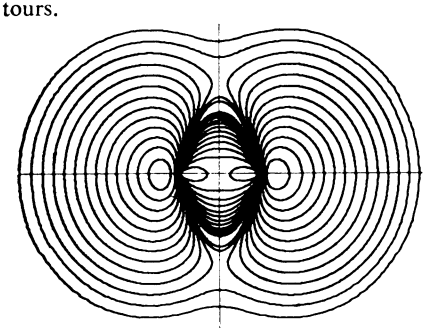


Fig. 25. Nitrogen 3 Sigma G Orbital Contours.

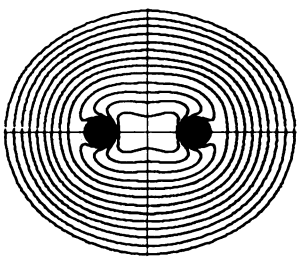


Fig. 29 (left). Oxygen Molecule 2 Sigma G Orbital Contours. Fig. 31 (right). Oxygen Molecule 1 P1 U Orbital Contours.

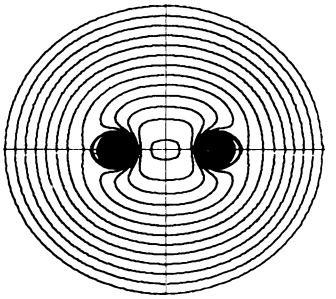


Fig. 16. Carbon Molecule 2 Sigma G Orbital Contours.

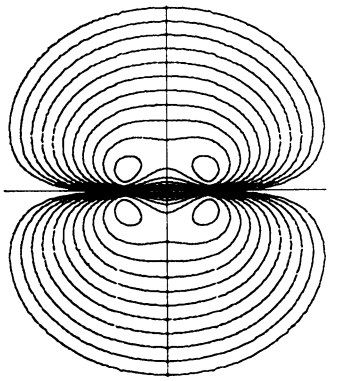


Fig. 18. Carbon Molecule 1 P1 U Orbital Contours.

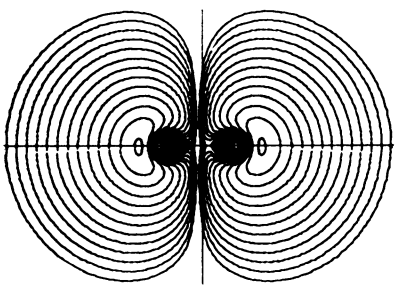


Fig. 23. Nitrogen 2 Sigma U Orbital Contours.

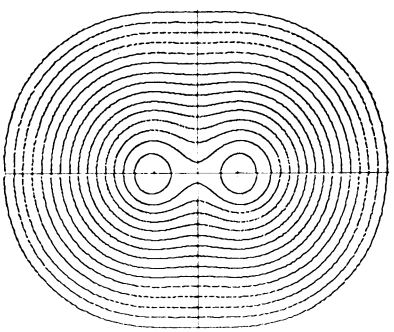


Fig. 26. Oxygen Molecule Total Electron Density Contours.

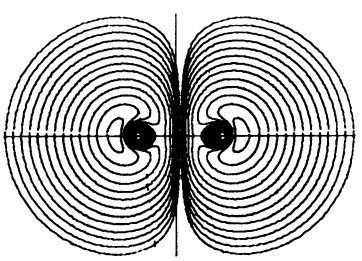


Fig. 30 (center). Oxygen Molecule 2 Sigma U Orbital Contours.

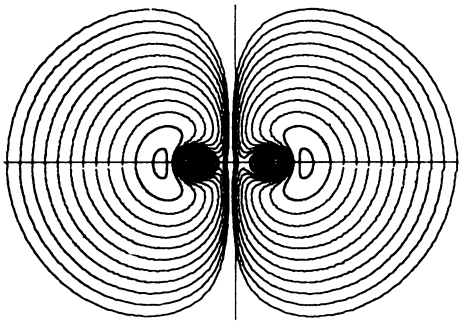


Fig. 17. Carbon Molecule 2 Sigma U Orbital Contours.

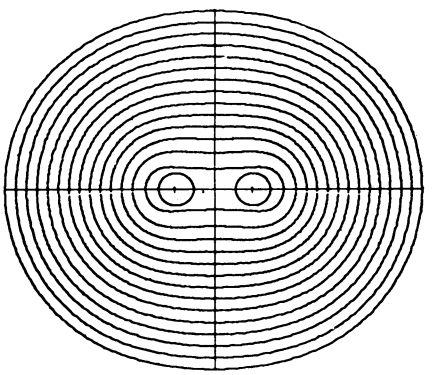


Fig. 19. Nitrogen Molecule Total Electron Density Contours.

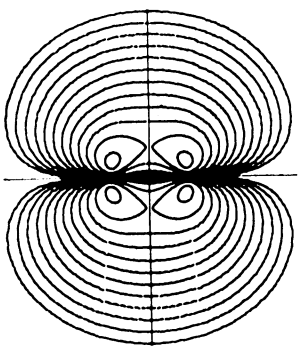


Fig. 24. Nitrogen 1 P1 U Orbital Contours.

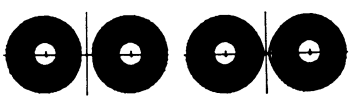
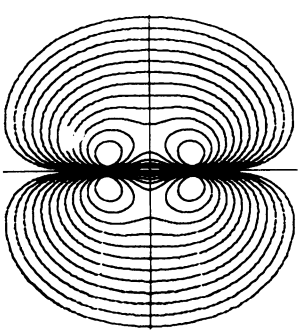


Fig. 27 (left). Oxygen Molecule 1 Sigma G Orbital Contours. Fig. 28 (right). Oxygen Molecule 1 Sigma U Orbital Contours.



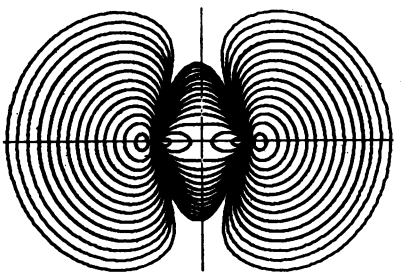


Fig. 32. Oxygen Molecule 3 Sigma G Orbital Contours.

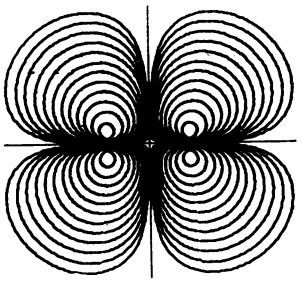


Fig. 33. Oxygen Molecule 1 P1 G Orbital Contours.

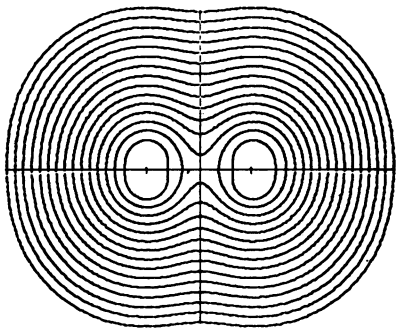


Fig. 34. Fluorine Molecule Total Electron Density Contours.

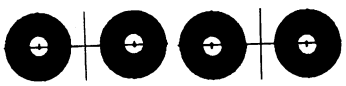


Fig. 35 (left). Fluorine Molecule 1 Sigma G Orbital Contours. Fig. 36 (right). Fluorine Molecule 1 Sigma U Orbital Contours.

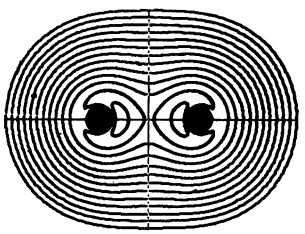


Fig. 37. Fluorine Molecule 2 Sigma G Orbital Contours.

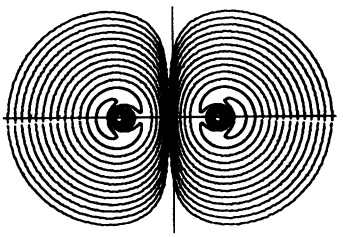
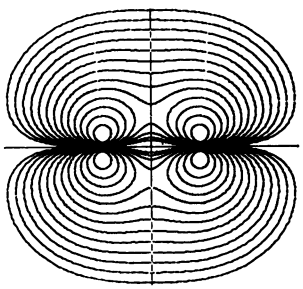
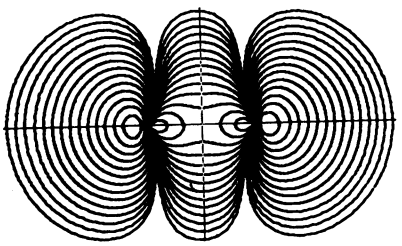


Fig. 38. Fluorine Molecule 2 Sigma U Orbital Contours.





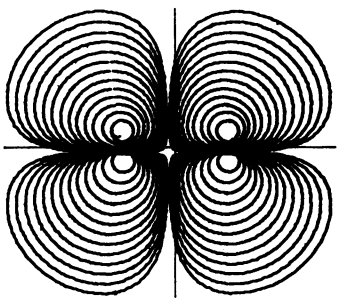


Fig. 39 (left). Fluorine Molecule 1 P1 U Orbital Contours. Fig. 40 (center). Fluorine Molecule 3 Sigma G Orbital Contours. Fig. 41 (right). Fluorine Molecule 1 P1 G Orbital Contours.

then plotted between adjacent points, thus yielding as computer time exposures the smooth contour curves displayed in the figures. For the total density Eq. 9 and its derivatives were used.

The input to the program consists of the symmetry basis functions $\chi_{p\lambda\alpha}$, the orbital coefficients $C_{ip\lambda}$ (*10*), the internuclear distance R, a series of the contour values desired with the associated thresholds, and finally, the physical scale in which diagrams are to be plotted. The output consisted of 35-millimeter negative films of the diagrams presented here.

Results and Implications

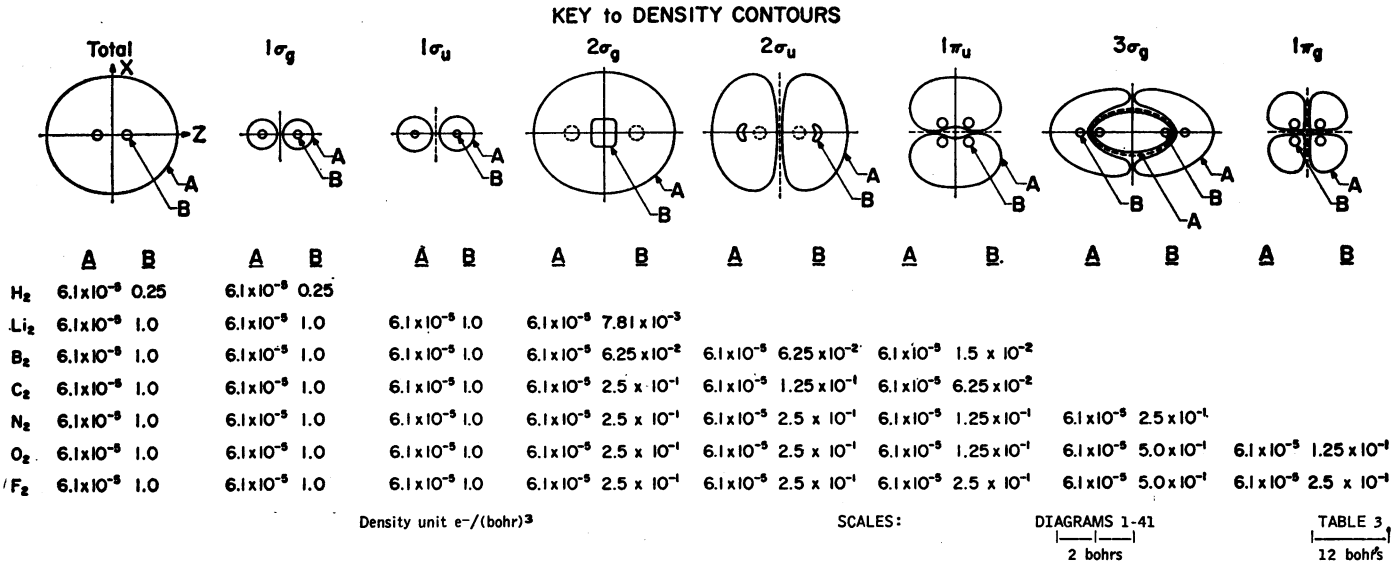
In the figures the contours of density associated with the homonuclear diatomic molecules constructed from first-row atoms are given on a consistent basis as defined in the key (Table 2). Both the total molecular densities and the orbital densities are displayed.

A shell may certainly be visualized in terms of these distributions of the electrons assigned to that shell. In the contour diagrams (figures) the difference between shells is clear as the difference in the value of electronic density in corresponding regions of space and in the overall pattern of contours. The difference between the same shells in different molecules is also of interest. See Table 3 and the following groups of diagrams: Figs. 1, 3, 7, 13, 19, 26, and 34; Figs. 2, 4, 8, 14, 20, 27, and 35; Figs. 5, 9, 15, 21, 28, and 36; Figs. 6, 10, 16, 22, 29, and 37; Figs. 11, 17, 23, 30, and 38; Figs. 12, 18, 24, 31, and 39; Figs. 25, 32, and 40; Figs. 33 and 41 (*11*).

I hope that, in addition to their teaching value, these contour diagrams of the shell model for these simple homonuclear diatomic molecules, H_2, Li_2, B_2, C_2, N_2, O_2, and F_2 will be useful symbols which will stimulate thought about chemical binding, steric hindrance, and bonding and antibonding orbitals, in addition to providing a correct and more complete picture of the shell model where only a rudimentary one, based primarily on hydrogen-atom wave functions, existed before.

A number of concepts and changes are best presented visually, but such visual presentations have been quite limited in the past because the labor involved was prohibitive (*6, 9*). The completely automatic programs developed now make it easy to visually analyze a very large amount of calculated data. Studies of interatomic forces and the formation of the chemical bond are underway in which these programs are being used to display the changes occurring in electronic charge density as a molecule forms (*12*).

In a study of molecular ionization these automatic contour programs are being used to illustrate directly changes in the molecular charge distribution which results from electron removal. In other theoretical work, a pictorial display of configuration mix-



	Total A	Total B	$1\sigma_g$ A	$1\sigma_g$ B	$1\sigma_u$ A	$1\sigma_u$ B	$2\sigma_g$ A	$2\sigma_g$ B	$2\sigma_u$ A	$2\sigma_u$ B	$1\pi_u$ A	$1\pi_u$ B	$3\sigma_g$ A	$3\sigma_g$ B	$1\pi_g$ A	$1\pi_g$ B
H_2	6.1×10^{-5}	0.25	6.1×10^{-5}	0.25												
Li_2	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	7.81×10^{-3}								
B_2	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	6.25×10^{-2}	6.1×10^{-5}	6.25×10^{-2}	6.1×10^{-5}	1.5×10^{-2}				
C_2	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	2.5×10^{-1}	6.1×10^{-5}	1.25×10^{-1}	6.1×10^{-5}	6.25×10^{-2}				
N_2	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	2.5×10^{-1}	6.1×10^{-5}	2.5×10^{-1}	6.1×10^{-5}	1.25×10^{-1}	6.1×10^{-5}	2.5×10^{-1}		
O_2	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	2.5×10^{-1}	6.1×10^{-5}	2.5×10^{-1}	6.1×10^{-5}	1.25×10^{-1}	6.1×10^{-5}	5.0×10^{-1}	6.1×10^{-5}	1.25×10^{-1}
F_2	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	1.0	6.1×10^{-5}	2.5×10^{-1}	6.1×10^{-5}	2.5×10^{-1}	6.1×10^{-5}	2.5×10^{-1}	6.1×10^{-5}	5.0×10^{-1}	6.1×10^{-5}	2.5×10^{-1}

Density unit $e^-/(\text{bohr})^3$

SCALES: DIAGRAMS 1-41 — 2 bohrs; TABLE 3 — 12 bohrs

Table 2. Value of contours. The diagrams indicate the general structure of each plot (Figs. 1–41). *A* labels the lowest contour value *plotted* and *B* the highest contour value *plotted* in each molecule [except for the contours which rise to a value of 1.0 $e^-/(\text{bohr})^3$ inside the $2\sigma_g$ and $2\sigma_u$ node]. Adjacent contour lines differ by a factor of 2. Thus all contours plotted are members of the geometric progression 2^{-N} $e^-/(\text{bohr})^3$ where N runs from 0 to 14. All plots are in a plane passing through the two nuclei. Dotted lines indicate nodal surface.

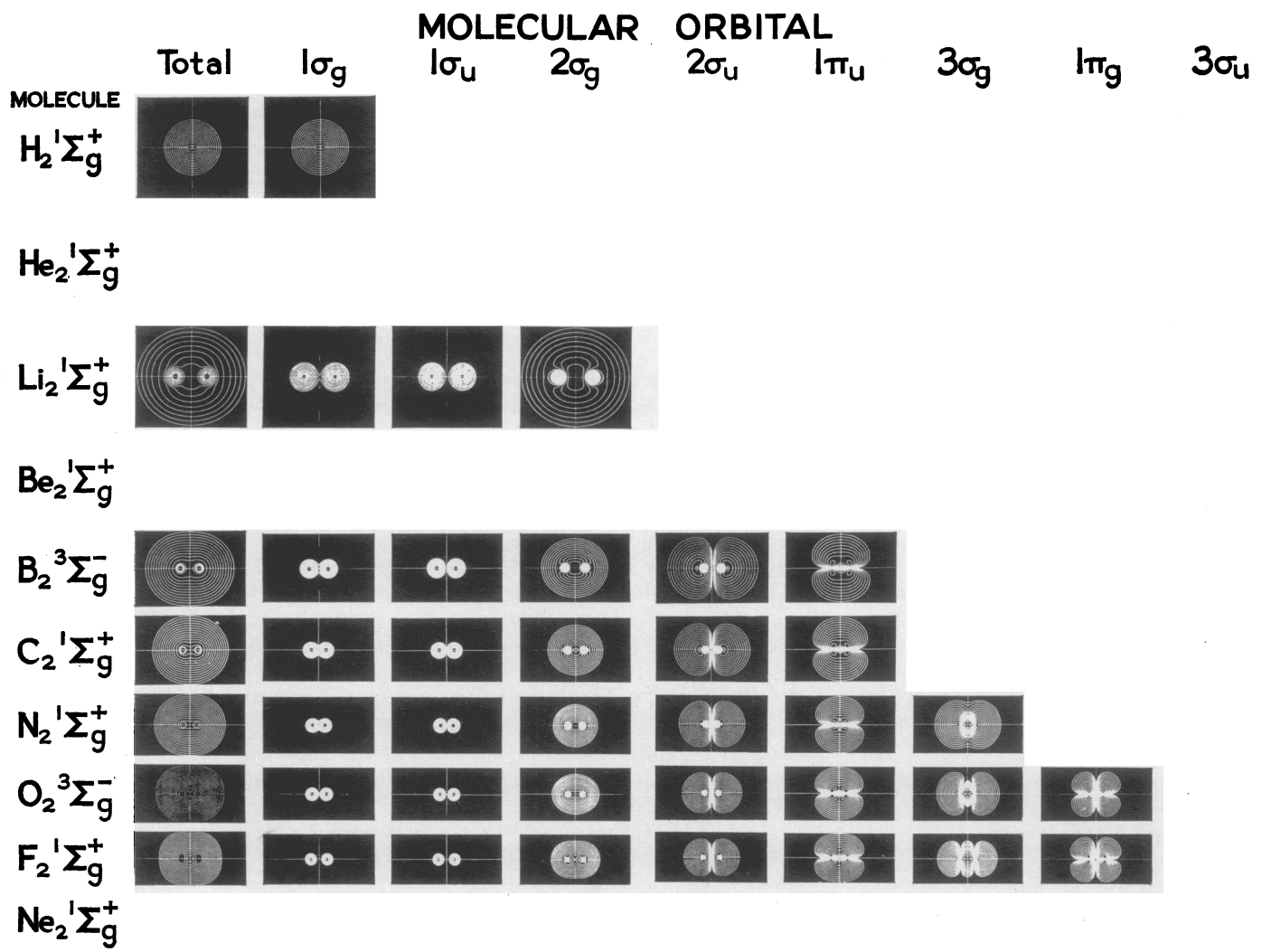


Table 3. The shell model of molecules. This chart consists of contour diagrams of the electron densities characteristic of the shell model of the molecules H_2, Li_2, B_2, C_2, N_2, O_2, and F_2. Both the total molecular density and the constituent shell densities are displayed at the experimental internuclear distance of each molecule. (He_2, Be_2, and Ne_2, which are members of this homonuclear series, are not bound in their ground state and therefore not displayed.)

ing is also in progress which provides a physical picture of wave function improvements and electron correlation as produced by added optimal configurations (*13*).

This work contains the development of a new tool, namely, the synthesis of programming skill, high-speed digital computers, and linked analog devices into a medium capable of efficiently communicating certain types of new information. Since many of us involved in large-scale computational efforts are often swamped by our own computer output and are able to competently analyze only a small fraction of the potentially useful information we have generated, this problem of communication is well worth consideration.

References and Notes

1. R. S. Mulliken, *Phys. Rev.* **41**, 49 (1932). For extensive references and detailed discussion, see J. C. Slater, *Quantum Theory of Molecules and Solids*: vol. 1, *Electronic Structure of Molecules* (McGraw-Hill, New York, 1963); G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, Princeton, N.J., ed. 2, 1950), chap. 6; and C. A. Coulson, *Valence* (Oxford Univ. Press, Oxford, ed. 2, 1961), chaps. 4–6.
2. A. C. Wahl, *J. Chem. Phys.* **41**, 2600 (1964).
3. ———, P. E. Cade, C. C. J. Roothaan, *ibid.* **41**, 2578 (1964).
4. C. C. J. Roothaan and P. S. Bagus, *Atomic Self-Consistent Field Calculations by the Expansion Method*; vol. 2, *Methods in Computational Physics* (Academic Press, New York, 1963).
5. C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951); **32**, 179 (1960).
6. W. Huo, *J. Chem. Phys.* **43**, 624 (1965).
7. P. E. Cade, K. D. Sales, A. C. Wahl, *J. Chem. Phys.*, in press; ———, in preparation; G. L. Malli and P. E. Cade, in preparation; J. B. Greenshields, in preparation.
8. A. C. Wahl and T. L. Gilbert, *Bull. Am. Phys. Soc.* **10**, 1097 (1965).
9. S. Peyerimhoff, *J. Chem. Phys.* **43**, 998 (1965).
10. The wave functions used in this study are available from the author on request. The F_2 function is given in (*2*). Others will appear soon with the studies of each individual molecule. All of the functions used are thought to be very near the Hartree-Fock wave function of each system. The Hartree-Fock charge distribution has been shown to be a representation of the exact charge distribution to first order in perturbation theory by Brillouin [*Actualitiés sci. et ind.* **71** (1933); *ibid.* **159** (1934)].
11. A single, large chart, similar to Table 3, has been prepared and is available from the author. For greater detail see Argonne National Laboratory Technical Report No. 7076.
12. T. L. Gilbert and A. C. Wahl, in preparation.
13. G. Das and A. C. Wahl, *J. Chem. Phys.*, in press.

14. Based on work performed under the auspices of the USAEC. I thank the Laboratory of Molecular Structure and Spectra for releasing the B_2 and C_2 wave functions prior to publication and the Computation Center Staff of the CDC 3600 computer and the Applied Mathematics Division at Argonne National Laboratory for processing these calculations, maintaining the DD 80 plotter, and providing library programs.

NEWS AND COMMENT

New York's New Mayor Enlists a Panel of Scientific Advisers

New York, N.Y.—In addition to noise, clotted traffic, filthy air, grime, a rising crime rate, and other accepted burdens of city life, New Yorkers in the recent past have experienced a water shortage; an outbreak of violence in the long, hot summer of '64 that approached civil insurrection; a series of strikes that at different times banished newspapers, shut the schools, and paralyzed public transport; and, of course, the big blackout. They also held an election which resulted in an upset victory in the mayoralty race, attributable, in a degree nobody will ever calculate, to voter exasperation over these vicissitudes.

The new mayor, Republican John V. Lindsay, occupies office in a splendid isolation produced by the ticket splitting which left him to preside over an administration in which the other elected officials are mostly Democrats. Lindsay, on top of everything else, is mayor of a city afflicted with a continuing and serious financial crisis. The new mayor's resourcefulness is, therefore, being put to a stern test, and one of his innovations has been creation of a Scientific and Technical Advisory Council.

The existence of such a council has the double advantage of making outside expert advice available on scientific and technical matters and, because of its stellar membership, of providing Lindsay with a link to major corporations, universities, and foundations in the city.

Lindsay announced formation of the council in December, while still mayor-elect. The publicity release at the time noted, "The work of the council will be primarily aimed at attracting and assisting science-oriented industry into the City's future economy." Lindsay said he also expected the council to advise him on the city's massive problems of health, air and water pollution, and transportation.

As a congressman with a liberal voting record through three and a half terms of service in Washington, Lindsay reflects a view of the dynamics of economic development which has become almost standard in Congress in the last few years.

In announcing formation of the council he combined an expression of this view with the rhetoric expected of a newly elected official when he observed that "our industries must be kept informed of technological innovation and prepare themselves for fruitful participation. Our educational and training programs must be constantly reviewed and revised and brought into line with changing developments. Our work force must seize novel challenges with new enlightenment and our financial institutions must embrace bold concepts of creative capitalism."

Going on to cite the benefits of science-oriented industry, Lindsay struck another familiar chord when he noted that federal expenditures for science have soared and that "many communities across the country have benefited immensely from this massive injection of federal funds." But, he said, "New York City has been short-changed. New York City—which has half the manufacturing employees in the State—has not received its fair share of federal expenditures."

The inspiration and model for the new council, not surprisingly, were also Washingtonian. The concrete proposal for creation of the council came from Detlev W. Bronk, president of the Rockefeller University, and in conjunction with John R. Dunning, dean of the school of engineering and applied science at Columbia, both of whom are very familiar with the corridors of scientific advice in Washington. Lindsay immediately took up the idea and appointed both to the council. Dunning serves as chairman.*

The council is intended to be, not a task force, but, rather, a continuing entity. Its method of operation will take some time to evolve, however, and it is, of course, too early to predict how effective the group will be.