

Theoretical Determination of the Electron Distribution in Benzene by the Thomas-Fermi and the Molecular-Orbital Methods

BY N. H. MARCH*

Wheatstone Physics Laboratory, King's College, London W.C. 2, England

(Received 23 August 1951)

The results of theoretical calculations of the electron distribution in benzene are reported. Density contours, both in the plane of the benzene ring and in a parallel plane at a height of 0.35 Å above the ring, are given for the Thomas-Fermi and the molecular-orbital methods. It is shown that in the molecular-orbital method the π electrons have only a small influence on the density in the parallel plane, except immediately above the carbon atoms, where they contribute about half of the total density. As far as comparison is valid the results appear to be in reasonable agreement with X-ray results of Robertson and his co-workers for naphthalene.

1. Introduction.

Interest in the problem of calculating theoretically the electron distribution in organic molecules has been aroused by recent accurate X-ray results (Abrahams, Robertson & White 1949 *a, b*; Mathieson, Robertson & Sinclair 1950 *a, b*) giving the density distributions in naphthalene and anthracene.

In view of the central position occupied by benzene, both in organic chemistry and in molecular theory, it was decided at the outset to make a detailed investigation of the electron distribution in benzene, rather than tackle at first the necessarily lengthier calculations for naphthalene and anthracene. Whilst no results exist as yet for benzene, a significant comparison can already be made with the experimental results quoted above. The extension of the work described here to the cases of naphthalene and anthracene would be straightforward but very laborious.

The electron distribution in benzene reported here has been calculated by two quite distinct methods. First the statistical method of Thomas and Fermi has been used, and secondly a full calculation has been carried out using the molecular-orbital method. As the Thomas-Fermi (T.F.) method does not make the usual distinction of molecular theory between π and σ electrons, it seemed that this method might be of value as a pointer to the validity of other treatments.

2. Use of the Thomas-Fermi method

Besides the intrinsic interest attached to the electron distribution in benzene the application of the T.F. method is of some interest from the point of view of the statistical theory and the method will thus be described in some detail.

As is well known, the T.F. method in atomic theory gives a useful overall representation of the electron density in heavy atoms. However the method has been restricted in its application to molecules by the mathematical difficulties presented by the non-linear character of the fundamental equation. The only direct attempt to solve the T.F. equation for a molecule has been made by Hund (1932), who has shown how a fairly good approximate solution can be obtained in the case of diatomic molecules. At the outset it was not of course clear whether Hund's method could be extended to systems other than those with axial symmetry; this work seems to show that the method can be successfully extended to our case.

3. Simplification of the problem

In the treatment of any neutral molecule by this method the fundamental problem is to solve the T.F. equation (see for example, Mott & Sneddon, 1948, p. 156)

$$\nabla^2 V = \mu V^{\frac{3}{2}}, \quad (1)$$

where

$$\mu = \frac{32\pi^2 e}{3h^3} (2me)^{\frac{3}{2}},$$

for the electrostatic potential V , subject to the conditions that as any nucleus is approached, V tends to the Coulomb potential due to that nucleus and that V tends to zero at infinity.

It must be admitted that to some extent benzene is not well suited to a T.F. treatment owing to the presence of hydrogen atoms where the small concentration of electrons renders any statistical method unreliable. Thus, even in the event of an exact solution of equation (1) being possible for benzene, the results would have to be regarded with due caution and probably the only regions in which any useful conclusions could be drawn would be in the regions between adjoining carbon nuclei, and in

* Present address: Department of Physics, The University, Sheffield, England.

the interior of the ring, where the effect of the hydrogen atoms would be exceedingly small. In view of this, and of a lack of knowledge as to the applicability of Hund's method of solution except in diatomic cases, it was decided at the outset to simplify the problem as follows. A neutral system of thirty-six electrons and six carbon nuclei arranged as in benzene is to be considered and the distribution of charge resulting from the T. F. equation investigated. The assumption is made that when the distribution in this system is known, then by simply adding to it the charge density contributions from six hydrogen atoms placed in their appropriate positions, an approximate distribution is obtained for benzene. Physically one would expect this approximation to have a negligible effect on the electron distribution in the interior of the ring and in the region between the carbon atoms, but that the C-H bonds would not be adequately described in the sense of the T. F. method (which at any rate, as we shall see later, does not cause enough charge to be pushed into the centre of a bond to give a completely adequate description).

4. Method of solution

By working in units of R , the half distance between neighbouring carbon nuclei, and in terms of the dimensionless function u defined by

$$V = \frac{Ze}{R} u,$$

equation (1) transforms to

$$\nabla^2 u = \gamma u^{\frac{3}{2}}, \quad (2)$$

where

$$\gamma = \mu(ZeR^3)^{\frac{1}{2}}.$$

In our case $2R$ is taken to be 1.39 \AA , and then $\gamma = 4.44$.

Following Hund, an approximate solution is sought of the form

$$u = v(r_1) + v(r_2) + \dots + v(r_6), \quad (3)$$

where r_1, \dots, r_6 denote the distances of a point from nuclei 1, \dots , 6 respectively. In the neighbourhood of any one nucleus an approximate solution would be given by taking $v(r)$ simply as the solution for an atom, that is $(1/r)\varphi(\gamma^{\frac{2}{3}}r)$, where φ is the function calculated by Fermi, Bush & Caldwell, and Miranda, and conveniently tabulated by Gombás (1948, p. 358). However, with this form for $v(r)$, u would not satisfy the equation (2) at infinity for there the system behaves as a single atom of nuclear charge 36, and an asymptotic solution is

$$u = \frac{6}{r} \varphi(6^{\frac{1}{3}}\gamma^{\frac{2}{3}}r).$$

A solution is therefore assumed to be of the form

$$u = \frac{1}{r_1} \varphi(\gamma^{\frac{2}{3}}r_1 f(r_1)) + \frac{1}{r_2} \varphi(\gamma^{\frac{2}{3}}r_2 f(r_2)) + \dots + \frac{1}{r_6} \varphi(\gamma^{\frac{2}{3}}r_6 f(r_6)), \quad (4)$$

where

$$f(r) = \frac{\lambda^2 + 6^{\frac{1}{3}}r^2}{\lambda^2 + r^2}, \quad (5)$$

and the question to be answered is whether, for any value of λ , it can be made a reasonable approximate solution of the differential equation. Equation (5) corresponds to Hund's expression for $f(r)$ for diatomic molecules, and is one of the simplest expressions which will give the necessary asymptotic forms at the six nuclei and at infinity. With u of the form (3),

$$\begin{aligned} \nabla^2 u &= \nabla^2 v(r_1) + \nabla^2 v(r_2) + \dots + \nabla^2 v(r_6) \\ &= h(r_1) + h(r_2) + \dots + h(r_6). \end{aligned} \quad (6)$$

When

$$\begin{aligned} v(r) &= \frac{1}{r} \varphi(\gamma^{\frac{2}{3}}r f(r)), \\ h(r) &= \frac{\gamma[f(r) + r f'(r)]^2 v(r)^{\frac{3}{2}}}{f(r)^{\frac{1}{2}}} \\ &\quad + \gamma^{\frac{2}{3}} \left[\frac{2}{r} f'(r) + f''(r) \right] \varphi'(\gamma^{\frac{2}{3}}r f(r)). \end{aligned} \quad (7)$$

With $f(r)$ defined by (5),

$$f(r) + r f'(r) = \frac{\lambda^2[\lambda^2 + (6^{\frac{1}{3}} - 1)r^2] + 6^{\frac{1}{3}}r^4}{(\lambda^2 + r^2)^2}, \quad (8)$$

and

$$\frac{2}{r} f'(r) + f''(r) = \frac{2\lambda^2(6^{\frac{1}{3}} - 1)(3\lambda^2 - r^2)}{(\lambda^2 + r^2)^3}. \quad (9)$$

This enables us to calculate $\nabla^2 u$.

Next, as in Hund's work, the quantity B , defined by

$$B = \gamma u^{\frac{3}{2}} - \nabla^2 u, \quad (10)$$

was calculated at a number of suitable points for various values of λ , and the value of λ was sought for which B was as small as possible over the region considered. As the axial symmetry of Hund's problem was lacking here, a choice of planes in which to calculate B had to be made. It was decided to consider points in the plane of the benzene ring and also in a plane parallel to the plane of the ring. This choice was made, first to ascertain whether the best value of λ in one plane was the best value in the other, and secondly to facilitate comparison with the results of the molecular-orbital method. The distance of the parallel plane from the plane of the ring was taken as $0.5R$, (0.35 \AA), of the order of the height of the plane of maximum density of the π electrons above the plane of the ring in the molecular-orbital method. Calculations were made for $\lambda^2 = 4, 5, 6$, and it was found that $\lambda^2 = 5$ was the best compromise value in both planes. The value of λ thus obtained completely

defines the approximate solution (3) and hence the approximate density distribution. Unfortunately any estimate of the accuracy of the solution would be difficult.

5. Choice of λ^2

As the value of λ completely defines the approximate solution, a little more will be said here about the choice. Without detailed tables or elaborate contours, which are clearly not justified here, it is difficult to display the various results for B . The following qualitative summary should however suffice to show that a reasonable choice can be made.

Dividing the regions of space somewhat artificially into that inside the ring and that outside the ring, the following conclusions could be drawn:

(1) At 'internal' points in the plane of the ring a value 5 for λ^2 was slightly better than 4, 6 being certainly the worst value.

(2) At 'internal' points in the parallel plane 5 was clearly better than 4 or 6.

(3) At 'external' points in both planes $\lambda^2 = 6$ was found to be the best value, 4 being certainly the worst.

It is not difficult to see from these results that a change for the worse results in going from 5 to either 4 or 6, and that $\lambda^2 = 5$ is the best compromise value that can be obtained by this method. To give some indication of the magnitudes of the differences B , the mean values of $|B|/\gamma u^{\frac{1}{2}}$ have been evaluated for the various points considered for $\lambda^2 = 5$. In the order in which the regions are referred to above, the values are 0.032, 0.022, 0.123 and 0.159. These values suggest that the solution will be most reliable in the interior of the ring; which is satisfactory in view of the method of accounting for the hydrogen atoms adopted here. Also it is satisfactory that as far as it is possible to compare them, the trends in the values of B agree well with those found by Hund for the case of diatomic molecules.

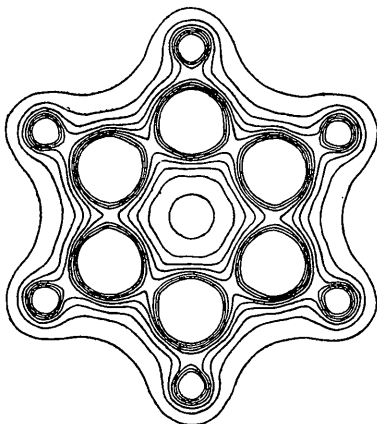


Fig. 1. T.F. electron-density contours in plane of ring. Outer contour is $0.15 \text{ e.}\text{\AA}^{-3}$, interval is $0.2 \text{ e.}\text{\AA}^{-3}$. Density is infinite at all nuclei and to avoid complicating the figure contours finish at $1.35 \text{ e.}\text{\AA}^{-3}$ round the hydrogen atoms and at $1.75 \text{ e.}\text{\AA}^{-3}$ round the carbon atoms.

6. The approximate distribution in benzene

Remembering the assumption made at the outset, the charge density due to six hydrogen atoms, with their nuclei placed as in benzene, must be added to the density already obtained. The T.F. method, applicable to heavy atoms, obviously has little justification for

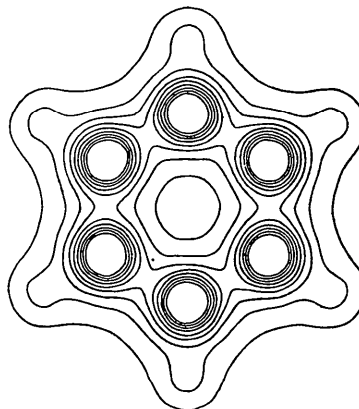


Fig. 2. T.F. electron-density contours in a plane parallel to the ring and at a height of 0.35 \AA above the plane of the ring. Outer contour is $0.15 \text{ e.}\text{\AA}^{-3}$, interval is $0.2 \text{ e.}\text{\AA}^{-3}$. Density is $0.5 \text{ e.}\text{\AA}^{-3}$ immediately above the hydrogen atoms, and above the carbon atoms $3.8 \text{ e.}\text{\AA}^{-3}$. Last contour shown is $1.75 \text{ e.}\text{\AA}^{-3}$.

hydrogen. A comparison of the radial charge density for hydrogen given by wave mechanics and by the T.F. method shows, however, that the two are considerably but not wildly different; and to avoid introducing functions foreign to the T.F. method the T.F. density was used. In any case, any conclusions drawn will be to a large extent independent of this, since the only regions that will be discussed are between the carbon nuclei and inside the ring. The charge contours in the plane of the ring are shown in Fig. 1, and those for the parallel plane in Fig. 2.

7. General outline of the molecular-orbital method

The principle of the second method used here, namely, the molecular-orbital method, can be described very simply as follows. Each individual electron is assigned a wave function and the total wave function is constructed as a determinant, in the usual way, from the one-electron wave functions, the total wave function thus constructed being antisymmetrical in the electrons. If the total wave function is denoted by $\Psi(r_1 \dots r_n)$, where r_j represents all the coordinates of the j th electron, then the charge density due to electron 1 will be given by

$$\rho(1) = \int |\Psi|^2 d\tau_2 \dots d\tau_n, \quad (11)$$

with suitable normalisation of Ψ such that

$$\int \rho(1) d\tau_1 = 1. \quad (12)$$

From the form of the total wave function it follows that the charge density due to any other electron will be given by an exactly similar expression, so that the total density can be obtained.

8. Construction of one-electron functions

The 1s electrons of the carbon atoms are assumed to be unchanged by the formation of the molecule, and hence supply the first one-electron functions. To obtain the other one-electron functions needed, the 2s and 2p carbon atomic orbitals are first hybridized in the usual manner to form trigonal orbits. It is

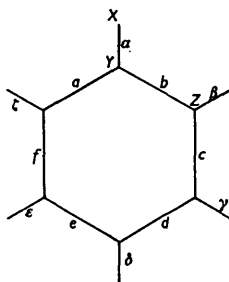


Fig. 3. Notation for the bond orbitals.

now assumed that 'molecular orbitals' (m.o.'s) which serve as the one-electron wave functions in the total wave function, can be formed in the usual way by linear combination of atomic orbitals.

Thus, for example, the m.o. based on bond Y-Z (see Fig. 3) and designated by b , can be written

$$b = \psi_Y(tr_{YZ}) + \psi_Z(tr_{ZY}), \quad (13)$$

where $\psi_Y(tr_{YZ})$ denotes the trigonal orbit based on nucleus Y and directed along YZ. The form of $\psi_Y(tr)$ is given by

$$\psi_Y(tr_{YZ}) = \frac{1}{\sqrt{3}} \{ \psi_Y(2s) + (\sqrt{2})\psi_Y(2p_{YZ}) \}, \quad (14)$$

where $\psi_Y(2s)$ and $\psi_Y(2p_{YZ})$ are the 2s and 2p atomic orbitals of carbon. In a similar way the m.o.'s based on the C-H bonds can be formed. These are assumed to be of the form

$$\alpha = \psi_Y(tr_{YX}) + \psi_X(1s), \quad (15)$$

where $\psi_X(1s)$ is the 1s hydrogen wave function. If the coefficient of $\psi_X(1s)$ in this orbital were changed slightly from unity, to allow a possible small polarity in the C-H bonds, the distribution in the C-H bonds would be slightly altered but the distribution between the carbon atoms and in the interior of the ring would almost certainly be negligibly affected. Each of these orbitals has axial symmetry about the particular bond on which it is based; they are the σ orbitals. From the 2p_z atomic wave functions (the z axis being perpendicular to the plane of the ring) additional orbitals, the π orbitals, are formed. These can be written in the form (Mayer & Sklar, 1938)

$$\left. \begin{aligned} \psi_0 &= (p_1 + p_2 + p_3 + p_4 + p_5 + p_6) \\ \psi_1 &= (p_1 + \omega p_2 + \omega^2 p_3 - p_4 - \omega p_5 - \omega^2 p_6) \\ \psi_2 &= (p_1 + \omega^2 p_2 - \omega p_3 + p_4 + \omega^2 p_5 - \omega p_6) \\ \psi_3 &= (p_1 - p_2 + p_3 - p_4 + p_5 - p_6) \\ \psi_4 &= (p_1 - \omega p_2 + \omega^2 p_3 + p_4 - \omega p_5 + \omega^2 p_6) \\ \psi_5 &= (p_1 - \omega^2 p_2 - \omega p_3 - p_4 + \omega^2 p_5 + \omega p_6) \end{aligned} \right\} (16)$$

where $p_1 \dots p_6$ denote the 2p_z orbitals based on Y, Z, etc., and $\omega = \exp(i\pi/3)$.

The electrons are then allocated as follows: two in each of the 1s orbits, a total of twelve being thus accommodated; two in each of the σ orbitals, twenty-four electrons being accommodated in these. Six electrons remain and in the ground state of the molecule, which we are considering here, the three π orbitals of lowest energy (ψ_0, ψ_1, ψ_5) are each doubly filled.

9. Atomic wave functions

For carbon, Slater wave functions have been used in the following calculations (Slater, 1930). A defect of these wave functions is that $\psi(2s)$ and $\psi(1s)$ are not orthogonal. In the present work this is remedied in part by writing for b , instead of (13)

$$b = n[\psi_Y(tr_{YZ}) + \psi_Z(tr_{ZY}) + \lambda\psi_Y(1s) + \lambda\psi_Z(1s)], \quad (17)$$

where λ is chosen so that b is orthogonal to $\psi_Y(1s)$ and $\psi_Z(1s)$, and n is the normalizing factor. Using Slater wave functions,

$$n = 0.542, \quad \lambda = -0.212.$$

Similarly, α is written in the form

$$\alpha = m[\psi_Y(tr_{YX}) + \psi_X(1s) + \mu\psi_Y(1s)], \quad (18)$$

where μ is chosen so that α is orthogonal to $\psi_Y(1s)$. It is found that

$$m = 0.543, \quad \mu = -0.205.$$

The 1s orbitals are now orthogonal to all the orbitals used in describing the molecule except that the 1s carbon orbital on atom r (say) is not strictly orthogonal to the 1s orbital on atom s , nor to the σ -bond orbitals which do not terminate on atom r . Such lack of orthogonalization will be small and can certainly be neglected with safety.

10. Expression for charge density

Let us denote the 1s functions by $s_1 \dots s_6$ and the π wave functions ψ_0, ψ_1, ψ_5 , by π_1, π_2 , and π_3 . The total wave function is now written in the usual determinantal form, in terms of $s_1 \dots s_6, \pi_1 \dots \pi_3, a \dots f$ and $\alpha \dots \zeta$. However $a \dots f, \alpha \dots \zeta$ are not orthogonal and in this form the problem cannot be easily handled. From a property of determinants, however, linear combinations of $a \dots f, \alpha \dots \zeta$ may be taken, and apart from a numerical factor multiplying it the determinant will be unchanged. Thus, still

unnormalized Ψ can be written in a determinantal form with $\varphi_1 \dots \varphi_{12}$ replacing $a \dots \zeta$, where $\varphi_1 \dots \varphi_{12}$ are suitable linear combinations of the $a \dots \zeta$. A convenient choice is

$$\left. \begin{aligned} \varphi_1 &= a+b+c+d+e+f \\ \varphi_2 &= a+\omega b+\omega^2 c-d-\omega e-\omega^2 f \\ \varphi_3 &= a+\omega^2 b-\omega c+d+\omega^2 e-\omega f \\ \varphi_4 &= a-b+c-d+e-f \\ \varphi_5 &= a-\omega b+\omega^2 c+d-\omega e+\omega^2 f \\ \varphi_6 &= a-\omega^2 b-\omega c-d+\omega^2 e+\omega f \end{aligned} \right\} \quad (19)$$

and similarly φ_7 to φ_{12} are formed with $\alpha \dots \zeta$ replacing $a \dots f$. It is then easily shown that the only non-orthogonalities occurring are between φ_j and φ_{j+6} , where $j = 1 \dots 6$, and a convenient notation is

$$\int \varphi_j^* \varphi_k d\tau = a_{j,k}. \quad (20)$$

From this point two procedures are possible. One is to use a method developed by Lennard-Jones (1931) for treating determinantal forms in which the one-electron functions are not orthogonal; the other is to proceed to form two new wave functions which are orthogonal, from φ_j and φ_{j+6} . The second procedure is the more convenient here though of course both lead to the same result. Thus, from the wave functions φ_j and φ_{j+6} a wave function

$$\chi_j = n_j(\varphi_j + \delta_j \varphi_{j+6}) \quad (21)$$

is constructed such that

$$\int (\varphi_j^* + \delta_j^* \varphi_{j+6}^*) \varphi_{j+6} d\tau = 0;$$

that is

$$a_{j,j+6} + \delta_j^* = 0,$$

or

$$\delta_j^* = -a_{j,j+6}, \quad \delta_j = -a_{j+6,j}, \quad (22)$$

and

$$1/|n_j|^2 = 1 + \delta_j a_{j,j+6} + \delta_j^* a_{j+6,j} + \delta_j^* \delta_j. \quad (23)$$

We introduce now the convenient notation

$$a_{j,j+6} a_{j+6,j} = A_{j,j+6}. \quad (24)$$

Then

$$1/|n_j|^2 = 1 - A_{j,j+6}. \quad (25)$$

Thus the wave functions χ_j , φ_{j+6} ($j = 1 \dots 6$) are mutually orthogonal, and the complete set of one-electron wave functions are now completely orthogonal (remembering the assumption about the $1s$ wave functions). Then the total charge density is given by

$$\rho = 2 \left[\sum_{j=1}^6 |s_j|^2 + \sum_{j=1}^3 |\pi_j|^2 + \sum_{j=1}^6 |\chi_j|^2 + \sum_{j=1}^6 |\varphi_{j+6}|^2 \right], \quad (26)$$

the factor 2 arising because all the orbits are doubly occupied. In this expression all the one-electron functions are assumed to be normalized. It is clear that if ρ is integrated over all space the value of the integral will then be 42, the total number of electrons in the system. From (21)

$$\sum_{j=1}^6 |\chi_j|^2 = \sum_{j=1}^6 \frac{\varphi_j \varphi_j^* + \delta_j \varphi_j^* \varphi_{j+6} + \delta_j^* \varphi_{j+6} \varphi_j + \delta_j^* \delta_j \varphi_{j+6} \varphi_{j+6}}{1 - A_{j,j+6}} \quad (27)$$

Introducing $\Phi_{j,k} = \varphi_j^* \varphi_k$, ρ can be written

$$\rho = 2 \left[\sum_{j=1}^6 |s_j|^2 + \sum_{j=1}^3 |\pi_j|^2 + \sum_{j=1}^6 \frac{\Phi_{j,j} + \Phi_{j+6,j+6} - (a_{j+6,j} \Phi_{j,j+6} + a_{j,j+6} \Phi_{j+6,j})}{1 - A_{j,j+6}} \right]. \quad (28)$$

11. Calculation of ρ

In order to calculate the overlaps $a_{j,j+6}$, the values of the overlaps between the original m.o.'s $a \dots f$, $\alpha \dots \zeta$, were needed. These were calculated using the wave functions described previously and are given below, $S_{\alpha\beta}$ denoting $\int \alpha\beta d\tau$; a and β being defined by equations (17) and (18).

$$\begin{array}{lll} S_{ab} = 0.1191 & S_{a\alpha} = 0.1307 & S_{\alpha\beta} = 0.1196 \\ S_{ac} = 0.0917 & S_{a\beta} = -0.0453 & S_{\alpha\gamma} = 0.0045 \\ S_{ad} = 0.0591 & S_{a\gamma} = -0.0100 & S_{\alpha\delta} = 0.0019 \end{array}$$

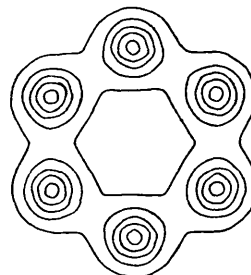


Fig. 4. π electron-density contours in a plane at a height of 0.35 Å above the plane of the ring. Outer contour is 0.15 e.Å⁻³, interval is 0.2 e.Å⁻³. All contours are shown.

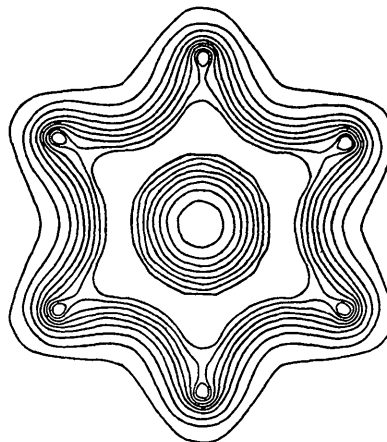


Fig. 5. Molecular orbital electron-density contours in the plane of the ring. Outer contour is 0.15 e.Å⁻³, interval is 0.2 e.Å⁻³. To facilitate comparison with the T. F. contours, last contour shown is 1.75 e.Å⁻³. The next contour, 1.95 e.Å⁻³, defines the separate carbon atoms.

The actual calculation was carried out in terms of $a \dots f, \alpha \dots \zeta$, so that ρ was written in terms of these wave functions. ρ was then evaluated on a mesh of points, first in the plane of the ring and then in a plane parallel to it. The π electrons make no contribution to the density in the plane of the ring since the wave functions describing them have nodes in this plane. The parallel plane was taken at a distance of $0.5R$

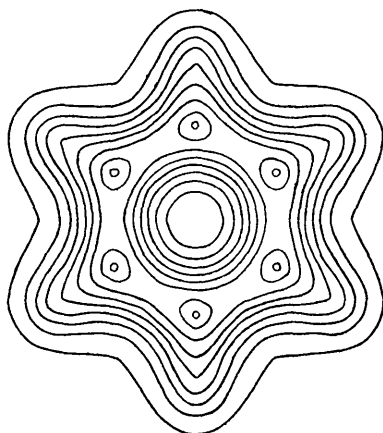


Fig. 6. Molecular orbital electron-density contours in a plane parallel to the plane of the ring and at a height of 0.35 \AA above the plane of the ring. Outer contour is $0.15 \text{ e.}\text{\AA}^{-3}$, interval is $0.2 \text{ e.}\text{\AA}^{-3}$. All contours are shown.

(0.35 \AA) from the plane of the ring; this is the same distance as in the T.F. calculation already described. The rather surprising feature is that even in this plane the density due to the σ and $1s$ electrons considerably outweighs that due to the π electrons, except immediately above the carbon atoms where the π electrons contribute about half of the total density. For interest the density contours due solely to the π electrons are shown in Fig. 4; the total density contours at intervals of $0.2 \text{ e.}\text{\AA}^{-3}$ are shown, for the plane of the ring in Fig. 5 and for the parallel plane in Fig. 6.

12. Comparison and discussion of results

If the contours for the total density as given by the two methods are compared the following conclusions can be drawn.

(i) Plane of ring

In the interior of the ring the variation of density given by the T.F. method is less rapid than that given by the m.o. method, as can be seen by the closer packing of the m.o. contours. The value at the centre of the ring is $0.29 \text{ e.}\text{\AA}^{-3}$ by the T.F. method and $0.20 \text{ e.}\text{\AA}^{-3}$ by the m.o. method. The positions of the $0.55 \text{ e.}\text{\AA}^{-3}$ and the $0.95 \text{ e.}\text{\AA}^{-3}$ contours inside the ring agree reasonably well with each other and also with the results obtained by Robertson for naphthalene. The bridge values, that is the values at the centre

of a line joining adjacent carbon atoms, are of some interest. The values given by the two different theoretical methods differ quite considerably, the T.F. method giving $1.2 \text{ e.}\text{\AA}^{-3}$ and the m.o. method giving $1.9 \text{ e.}\text{\AA}^{-3}$. Whilst it is not strictly permissible to compare these results with Robertson's values, one might suppose that the bond in naphthalene which would approximate most closely to a bond in benzene would be an end bond; this has a length of about 1.395 \AA , that is about the same length as that of a C-C bond in benzene, and it is farthest from the effect of the excess carbons in naphthalene over those in benzene. For these end bonds Robertson gives a value slightly in excess of $1.5 \text{ e.}\text{\AA}^{-3}$, a value which lies between the two theoretical values. One other point of some interest concerns the peak values at the carbon nuclei. With the T.F. model the density is infinite at the nuclei, a well known defect of the model. With the m.o. model the density is very large, around $830 \text{ e.}\text{\AA}^{-3}$. However, in these calculations it has been assumed that the atoms are fixed. Higgs (1951) has, however, recently shown that the effect of vibrations is to reduce greatly the peak value of the density, so that comparison of our results near the carbon nuclei with Robertson's is meaningless.

Not much can be said at the moment about the distribution external to the ring, except that the T.F. method will be unreliable in the region of the hydrogen atoms and will over-emphasize their presence. The work of Robertson gives the $0.5 \text{ e.}\text{\AA}^{-3}$ contour in rough outline only and comparisons will not be very significant. But the general agreement appears to be reasonable.

(ii) Parallel plane

The distributions here are quite similar to those in the plane of the ring. The peak values in this plane differ very considerably, $3.8 \text{ e.}\text{\AA}^{-3}$ by the T.F. method, $1.8 \text{ e.}\text{\AA}^{-3}$ by the m.o. method. The 'atoms' are much more pronounced again in the T.F. method than in the m.o. method, and the general variation of density is more rapid for the m.o. method. The 'bridge' values are for the T.F. method $0.81 \text{ e.}\text{\AA}^{-3}$ and for the m.o. method $1.5 \text{ e.}\text{\AA}^{-3}$ whilst the values at the centre are $0.25 \text{ e.}\text{\AA}^{-3}$ and $0.17 \text{ e.}\text{\AA}^{-3}$ respectively. A surprising feature of the m.o. results is the small contribution due to the π electrons, and in view of the close interpenetration of σ and π electrons it seems to us quite remarkable that precise calculations can be made of the properties of organic molecules in which only the π electrons are considered.

13. Conclusion

Considering the nature of the approximations involved in both the T.F. and the m.o. methods, and the difference in view point of the two methods, the distributions are in reasonable agreement with each other, and with the experimental results for

naphthalene as far as comparison is valid. The m.o. method seems to over-emphasize the amount of charge between the atoms, whilst the T.F. method tends to exaggerate the presence of the atoms at the expense of the 'bond' character. Also, as always, it should be remembered that the T.F. method gives poor results near the nuclei and at large distances, and that to some extent therefore charge contours 'flatter' its results. The results must await experimental work on the actual distribution in benzene before any more detailed discussion can be given of the relative merits of the two methods employed here.

It is a pleasure to thank Prof. C. A. Coulson for his most generous help and advice throughout the course of this work. The writer also wishes to acknowledge a grant from the Department of Scientific and Industrial Research.

References

- ABRAHAMS, S. C., ROBERTSON, J. M. & WHITE, J. G. (1949a). *Acta Cryst.* **2**, 233.
 ABRAHAMS, S. C., ROBERTSON, J. M. & WHITE, J. G. (1949b). *Acta Cryst.* **2**, 238.
 GOMBÁS, P. (1948). *Die Statistische Theorie des Atoms und ihre Anwendungen*. Vienna: Springer.
 HIGGS, P. W. (1951). Unpublished calculations.
 HUND, F. (1932). *Z. Phys.* **77**, 12.
 LENNARD-JONES, J. E. (1931). *Proc. Camb. Phil. Soc.* **27**, 480.
 MAYER, M. G. & SKLAR, A. L. (1938). *J. Chem. Phys.* **6**, 645.
 MOTT, N. F. & SNEDDON, I. N. (1948). *Wave Mechanics and its Applications*. Oxford: University Press.
 SINCLAIR, V. C., ROBERTSON, J. M. & MATHIESON, A. M. (1950a). *Acta Cryst.* **3**, 245.
 SINCLAIR, V. C., ROBERTSON, J. M. & MATHIESON, A. M. (1950b). *Acta Cryst.* **3**, 251.
 SLATER, J. C. (1930). *Phys. Rev.* **36**, 57.

Acta Cryst. (1952). **5**, 193

Particle Size Distribution from Small-Angle X-ray Scattering

BY JACOB RISEMAN

International Resistance Company, Philadelphia, Pa., U.S.A.

(Received 5 June 1951)

A solution of the integral equation describing the intensity of X-ray scattering at low angles by a non-uniform collection of independently scattering spherical particles is given. The final result is in a form such that the particle-size distribution can be calculated by integration. The resolvent kernel, which solves the integral equation, is shown to be a combination of half-integral order Bessel functions, and therefore obtainable from known tables. Utilizing the known scattering form for a single-sized group of spherical particles as illustration, the expected δ -function type of distribution is shown to result. The result obtained here can also be applied to the visible light scattering of dilute solutions of polydisperse macromolecules.

Introduction

During the past several years, small-angle X-ray scattering methods as a means for determining particle size have come into greater prominence. The theory of Guinier (1939, 1943, 1945; see also Hosemann 1939a, b), which served to interpret these results, was based on the independent scattering of a collimated, monochromatic beam by a system of equally sized spherical particles. The ideal character represented by such a set of assumptions, and the fact that one rarely encounters such systems within the laboratory, has stimulated research into such questions as the effect of particle shape, particle size distribution, and particle-particle interference (Patterson, 1939; Shull & Roess, 1947; Jellinek, Solomon & Fankuchen, 1946; Bauer, 1945; Roess, 1946; Yudowitch, 1949; Lund & Vineyard, 1949). Bauer (1945) and Roess (1946) have

derived methods for obtaining, by analytic means, the particle-size distribution from the corrected experimental data, and Jellinek, Solomon & Fankuchen (1946) have done likewise using an approximate geometric method.

The analytical expressions obtained in both these cases are fairly complex, and, so far as is known, have not been used for this purpose. We have therefore derived an expression which allows us to obtain the particle-size distribution by numerical integration. The assumptions used are similar to those mentioned above, i.e. spherical particles and negligible interference. To take also the latter into account would necessitate the introduction of a second distribution function, that of the interparticle distances. Analysis of a set of scattering data for these two parameters would become extremely difficult.