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A Comparison of Calculated and Measured Electron Distributions in the Benzene Ring

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The difference between the electron distribution in a molecule of benzene and that in an assemblage of unbonded carbon and hydrogen atoms, having the same coordinates and temperature factors as in the molecule, has been estimated by the method of molecular orbitals. The result is found to be in fairly good agreement with that determined experimentally by X-ray diffraction for the molecule of salicylic acid. In particular, the calculation appears to confirm the experimental evidence that the difference between the electron distributions of bonded and unbonded atoms is much smaller than a naive picture of a bond as a shared electron pair would indicate.

1. Introduction

Very few numerical calculations of the electron distribution in a molecule have been made, although methods of obtaining approximate wave functions for molecules are well known. March (1952) has calculated the electron distribution in benzene by both Thomas–Fermi and molecular-orbital methods. McWeeny (1952, 1953, 1954) has calculated scattering factors for bonded atoms, and from the method a molecular electron distribution could in principle be derived. There are correspondingly few instances in which the electron distribution has been measured with sufficient accuracy to make a comparison with theory worth while. March compared his results for the distribution in benzene with those obtained by Robertson and his collaborators for the distributions in naphthalene and anthracene (Abrahams, Robertson & White, 1949; Sinclair, Robertson & Mathieson, 1950). The calculations referred to a molecule without temperature motion, and in making the comparison with experiment only a qualitative allowance for this fact was made. No allowance was made for the fact that the measured distributions were obtained from X-ray diffraction data of limited range, and were thus affected by 'series-termination' errors.

The main features of the electron distribution in a molecule are closely approximated by a superposition of the electron distributions in the individual atoms, with allowance for temperature factor but without allowance for bonding. This is shown by the good agreement often obtained between observed and calculated X-ray structure factors, F_o and F_c, when the scattering factors appropriate to unbonded atoms are used in deriving the F_c's. It follows that some more sensitive method for the presentation of both theoretical and measured densities must be used if a valid comparison is to be made. In the presentation of measured density there are other good reasons for giving it as a difference between the actual density in the crystal and that appropriate to an assemblage of isolated unbonded atoms, having as far as possible the same coordinates and temperature factors as in the actual molecule (see, for example, Lipson & Cochran, 1953). When such a density map is prepared it is found that there is surprisingly little density in the bonds between atoms, and that if a hydrogen atom is not subtracted out it appears with an electron distribution almost indistinguishable from that of an isolated hydrogen atom. Comparison of such a map should be with a theoretical difference density, and in this paper such a density is given for benzene in a form comparable with experimental results for salicylic acid (Cochran, 1953). A difference density has been calculated both for a section in the plane of the ring and for a projection on to this plane. Only for the latter is a comparison with experiment possible as yet. Temperature motion of the molecule is allowed for, and series-termination errors are not important in difference densities.

2. Calculation of the difference density

The molecular-orbital method has been used, the atomic wave functions being those of Slater (1930), but including one of the improvements suggested by Duncanson & Coulson (1944). The atomic wave functions involved are thus, with distances measured in atomic units (1 a.u. = 0·5292 Å),

$$\begin{aligned}\psi^{\mathrm{H}}(1s) &= 0{\cdot}5642\ e^{-r} \text{ for hydrogen,}\\ \psi^{\mathrm{C}}(1s) &= 7{\cdot}6595\ e^{-5{\cdot}69r},\\ \psi^{\mathrm{C}}(2s) &= 1{\cdot}1243\ (re^{-1{\cdot}625r}-1{\cdot}5441\ e^{-5{\cdot}69r})\end{aligned}$$

and

$$\psi^{\mathrm{C}}(2p) = 1{\cdot}8992r\cos\theta\ e^{-1{\cdot}625r} \text{ for carbon.}$$

From these, the electron distribution ϱ^A, the sum of that in the isolated carbon and hydrogen atoms, can be calculated. The carbon atom has been taken to be in its prepared or valence state $(1s)^2(2s)^1(2p)^3$, for which the electron density has spherical symmetry.

As an abbreviation we write

$$(\psi^{C}(2s,2p))^2 = \tfrac{1}{4}[(\psi^{C}(2s))^2+(\psi^{C}(2p_x))^2+(\psi^{C}(2p_y))^2+(\psi^{C}(2p_z))^2]$$

To obtain the distribution ϱ^M in the molecule we follow the procedure of March (1952). A wave function is assigned to each individual electron, and from these a total wave function, antisymmetrical in the electrons, is constructed. The $(1s)$ orbitals of the carbon atoms are assumed not to change on bonding, and supply the first one-electron functions. Since they contribute equally to ϱ^A and to ϱ^M, they do not appear directly in our calculation of $\varrho^M-\varrho^A$. $\psi^C(2s)$ and $\psi^C(2p)$ are hybridized to form trigonal orbitals, and molecular orbitals are formed by linear combination of these trigonal orbitals with one another and with the $(1s)$ orbitals of the hydrogen atoms. Adapting March's notation, we take, for example, for the wave function of an electron in the σ bond between carbon and hydrogen atoms 1 (see Fig. 1)

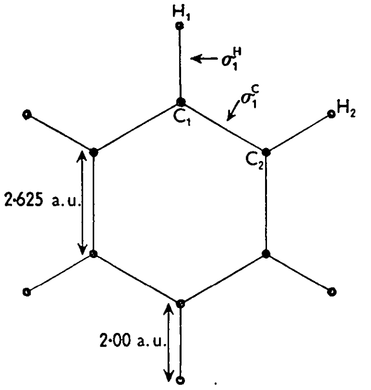

Fig. 1. Numbering of atoms, etc. in the molecule.

$$\sigma_1^H = M\left[\frac{1}{\sqrt{3}}(\psi_1^C(2s)+\sqrt{2}\,\psi_1^C(2p))+\psi_1^H(1s)+\mu\psi_1^C(1s)\right].$$

Here M is a normalizing constant, and μ is chosen to make σ_1^H orthogonal to $\psi_1^C(1s)$. Similarly, for the σ bond between carbon atoms 1 and 2 we have

$$\sigma_1^C = N\left[\frac{1}{\sqrt{3}}(\psi_1^C(2s)+\sqrt{2}\psi_1^C(2p)+\psi_2^C(2s)+\sqrt{2}\psi_2^C(2p)) +\lambda(\psi_1^C(1s)+\psi_2^C(1s))\right].$$

Each σ orbital contains two electrons. There are also three π orbitals, each being a linear combination of the six $(2p)$ orbitals which are perpendicular to the plane of the ring. The form of the combination has been given by Mayer & Sklar (1938). Each π orbital is doubly filled, and they are orthogonal to one another and to the σ orbitals. For the present we leave out of account the electrons in the π orbitals, as they do not contribute to the density in the plane of the ring—our first objective. The twelve $(1s)$ electrons are also ignored, for a reason already mentioned. We denote the remaining molecular density by ϱ^σ; it comprises 24 electrons. The expression for ϱ^σ can be derived by a very slight modification of the theory given by March (1952), followed by a numerical calculation. Where overlap integrals, normalizing constants, etc. were not already available from March's work, they were obtained with the help of the tables of Mulliken, Rieke, Orloff & Orloff (1949). The result obtained was

$$\begin{aligned}\varrho^\sigma = 2\sum_{j=1}^{6}\big(&\sigma_j^C\{1\cdot076\sigma_j^C-0\cdot001(\sigma_{j+1}^C+\sigma_{j+5}^C)\\ &\qquad-0\cdot189(\sigma_{j+2}^C+\sigma_{j+4}^C)+0\cdot079\sigma_{j+3}^C\}\\ &+\sigma_j^H\{1\cdot044\sigma_j^H-0\cdot003(\sigma_{j+1}^H+\sigma_{j+5}^H)\\ &\qquad-0\cdot126(\sigma_{j+2}^H+\sigma_{j+4}^H)+0\cdot128\sigma_{j+3}^H\}\\ &+\sigma_j^C\{-0\cdot266(\sigma_j^H+\sigma_{j+1}^H)+0\cdot174(\sigma_{j+2}^H+\sigma_{j+5}^H)\\ &\qquad+0\cdot010(\sigma_{j+3}^H+\sigma_{j+4}^H)\}\big).\end{aligned}\tag{1}$$

The evaluation of this expression, even with the help of an automatic calculating machine, would be a formidable task. In fact in this expression the only large terms are $(\sigma_j^C)^2$ and $(\sigma_j^H)^2$, and furthermore their coefficients are nearly unity. As an approximation, therefore, we take

$$\varrho^\sigma = 2\sum_{j=1}^{6}((\sigma_j^C)^2+(\sigma_j^H)^2);\tag{2}$$

that is, we treat the σ orbitals as if they were already orthogonal to one another. Later we estimate the effect of this approximation, which incidentally is also implicit in McWeeny's (1953, 1954) work. Use of (2) results in the great simplification that ϱ^σ is now composed of six functions having cylindrical symmetry about lines joining adjacent carbon atoms, and six having cylindrical symmetry about lines joining adjacent carbon and hydrogen atoms. The difference density can be similarly constructed; for example with carbon–hydrogen σ bond number 1 (Fig. 1) we associate a difference density

$$D_1^H = 2(\sigma_1^H)^2-(\psi_1^H(1s))^2-(\psi_1^C(2s,2p))^2;$$

that is, an electron in the hydrogen $(1s)$ atomic orbital is subtracted from one end of the bond and one 'valence state' electron from the other end. Similarly, with carbon–carbon σ bond number 1 we associate a difference density

$$D_1^C = 2(\sigma_1^C)^2-(\psi_1^C(2s,2p))^2-(\psi_2^C(2s,2p))^2.$$

The functions D^H and D^C also have cylindrical symmetry. A section through them is therefore all that has to be evaluated, and this was done using an automatic calculating machine, the EDSAC. Each function was evaluated over an area of about 40 a.u.^{2} on a square grid of spacing $\frac{1}{4}$ a.u., which took the machine about 80 min. The results are shown in Fig. 2. There is a density of $+1\cdot4$ e.Å^{-3} at the centre of a carbon–carbon bond, and of $-0\cdot36$ e.Å^{-3} on a line at 120° to this direction. For a carbon–hydrogen bond the corresponding figures are $+1\cdot0$ and $-0\cdot36$ e.Å^{-3}. The

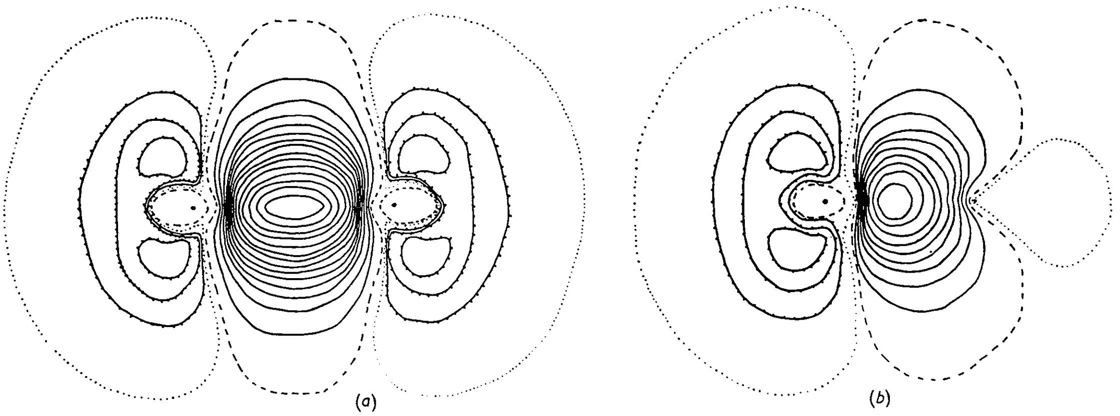

Fig. 2. (a) A section through the calculated difference density in a carbon–carbon σ bond. Atomic centres are marked by dots, and positive contours in their immediate neighbourhood have been omitted. The dotted lines represent densities of $\pm 0{\cdot}01$ e.Å^{-3}; other contours are at $-0{\cdot}3$, $-0{\cdot}2$, $-0{\cdot}1$, $+0{\cdot}1$, ..., $+1{\cdot}4$ e.Å^{-3}. (b) A section through the calculated difference density in a carbon–hydrogen σ bond. Contours as in (a), but the highest is $+0{\cdot}9$ e.Å^{-3}.

density exactly at the carbon nucleus is high, $+3{\cdot}7$ e.Å^{-3} in D^{H} for example, but this positive density is confined to a very small volume. However Figs. 2(a) and 2(b), taken by themselves, are apt to be misleading, as the separation which has been effected is of no real physical significance. On forming the total difference density

$$D^{\sigma} = \sum_{j=1}^{6} (D_j^{\mathrm{C}} + D_j^{\mathrm{H}}),$$

positive regions of one function tend to be cancelled by negative regions of others. The result for D^{σ} in the plane of the ring is shown in Fig. 3. The peak at the centre of the carbon–carbon bond is only $+0{\cdot}58$ e.Å^{-3} high, and the highest density along the carbon–hydrogen bond is $+0{\cdot}43$ e.Å^{-3}. Fig. 3 represents the theoretical difference density in the plane of the ring without allowance for temperature factor. A calculation has been made to estimate the effect of replacing (1) by the approximation (2). It is estimated that use of the exact expression would have increased the difference density of $+0{\cdot}58$ e.Å^{-3} at the centre of a carbon–carbon bond by not more than 15%, and would have reduced the difference density at the centre of the ring, for example, from $+0{\cdot}08$ e.Å^{-3} to almost exactly zero. The general picture would not be changed, and more than this cannot be expected to be correct in any case. In deriving Fig. 3 no account need be taken of the six electrons in π orbitals, except that, because of them, only three, and not four, electrons have been subtracted from each carbon atom at this stage.

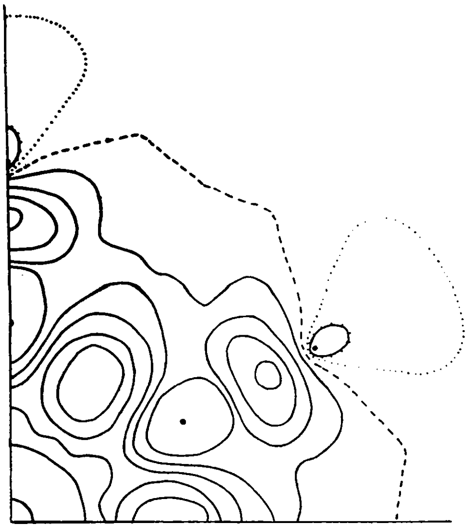

Fig. 3. Calculated difference density in the plane of the benzene ring. Contours as in Fig. 2, but the lowest is $-0{\cdot}1$ and the highest $+0{\cdot}5$ e.Å^{-3}.

For a comparison with measured values, a projection of the difference density, modified by an appropriate temperature factor, is required. This was obtained by calculating first the Fourier transforms of the functions D^{C} and D^{H}. Let x denote distance measured along the line joining two carbon atoms, and y distance measured in any direction at right angles. Let ξ and ζ be distances in corresponding directions in a reciprocal space. Only two coordinates are required in each case since both the function D^{C} and its Fourier transform T^{C} have cylindrical symmetry. It may readily be shown that

$$T^{\mathrm{C}}(\xi, \zeta) = \iint 2\pi y D^{\mathrm{C}}(x, y) J_0(2\pi y\zeta) \cos 2\pi x\xi \, dy\, dx\,. \quad (3)$$

This function was evaluated numerically, again using the EDSAC, for values of ξ and ζ between 0 and $1{\cdot}125$ a.u.$^{-1}$. A useful check was provided by the fact that $T^{\mathrm{C}}(0, 0)$ should be zero. Now, by a well known result in the theory of Fourier transforms, the projection of $D^{\mathrm{C}}(x, y)$ on a plane containing the x axis is the inverse transform of a section through $T^{\mathrm{C}}(\xi, \zeta)$ containing the ξ axis. Furthermore, the effect of temperature motion can be introduced by multiplying $T^{\mathrm{C}}(\xi, \zeta)$ by the temperature factor $\exp[-\alpha S^2]$, where $S^2 =$

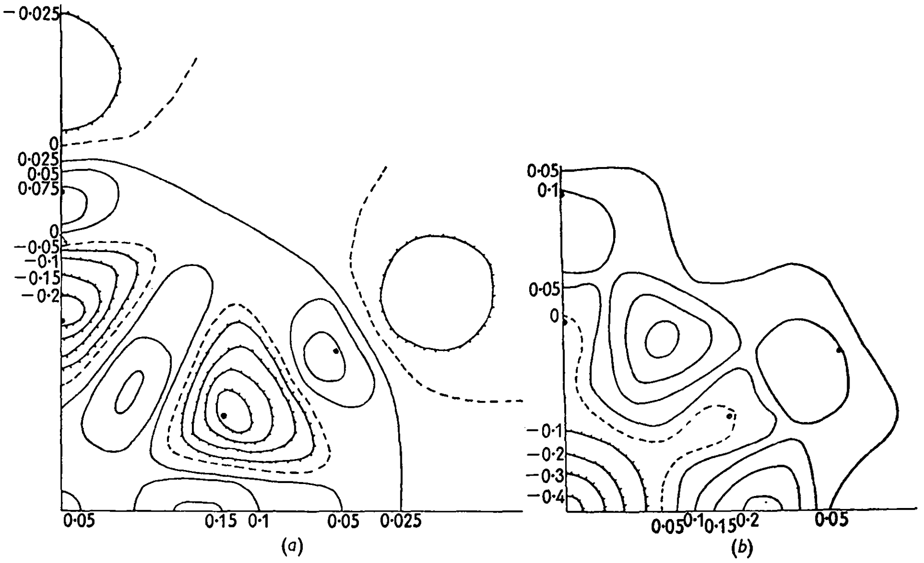

Fig. 4. (*a*) Calculated difference density in projection on the molecular plane, with allowance for temperature factor. (*b*) Measured density, for comparison with (*a*).

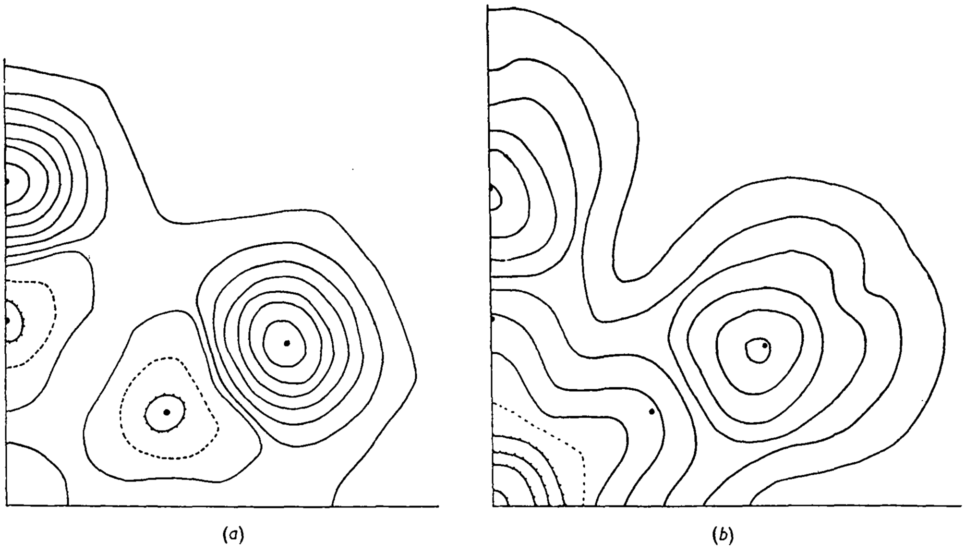

Fig. 5. (*a*) Calculated difference density in projection, without subtraction of the hydrogen atoms. Contours at an interval of 0·1 e.Å^{-2}. (*b*) Measured difference density, for comparison with (*a*). The outer 0 and 0·1 e.Å^{-2} contours cannot be drawn because of overlapping of adjacent molecules in the crystal.

$\xi^2+\zeta^2$, and $S = 2\sin\theta/\lambda$, in the usual notation of X-ray crystallography. The appropriate value of α, the average of that for the atoms of salicylic acid, is 3·2 a.u.^{2} and corresponds to a r.m.s. vibration in any direction of 0·4 a.u. (0·21 Å). (It is of course necessary to assume that the molecule moves as a rigid unit.) The projected difference density is now given by

$$d^{\mathrm{C}}(x, y) = \iint T^{\mathrm{C}}(\xi, \zeta) \exp\left[-\alpha(\xi^2+\zeta^2)\right] \times \cos 2\pi\xi x \cos 2\pi\zeta y \, d\xi \, d\zeta\,. \quad (4)$$

This function was evaluated as a two-dimensional Fourier series. The function d^{H} was evaluated in a similar way, but as D^{H} lacks a plane of symmetry perpendicular to the line joining the carbon and hydrogen atoms, cosine and sine transforms had to be evaluated separately at stage (3), and a corresponding change made at stage (4). The projected difference density is now

$$d^{\sigma} = \sum_{j=1}^{6} (d_j^{\mathrm{C}}+d_j^{\mathrm{H}})\,,$$

but to this the contribution of the electrons in π orbitals must be added.

Let $p_1, \ldots, p_6$ denote the $(2p_z)$ atomic orbitals of carbon atoms 1, ..., 6. A numerical calculation on the same basis as before leads to

$$\varrho^\pi = \sum_{j=1}^{6} \{p_j[0{\cdot}767p_j + 0{\cdot}489\,(p_{j+1}+p_{j+5}) - 0{\cdot}069\,(p_{j+2}+p_{j+4}) - 0{\cdot}347p_{j+3}]\}\,,$$

and therefore

$$D^\pi = \varrho^\pi - \sum_{j=1}^{6} (\psi_j^{\mathrm{C}}(2s, 2p))^2\,.$$

Terms in $p_j(p_{j+2}+p_{j+4})$ and p_jp_{j+3} make only a small contribution to D^π because of their small coefficients and/or the comparatively wide separation of the corresponding atoms, and have been neglected. The function d^π, representing D^π projected on the molecular plane with allowance for temperature effect, was evaluated by numerical methods which need not be described; they were broadly similar to those used to find d^{C} and d^{H}. The final result, for which we use the symbol d, is given by

$$d = d^\pi + d^\sigma\,,$$

and is shown in Fig. 4(*a*).

3. Comparison with experiment

The density shown in Fig. 4(*a*) is in agreement with that measured in salicylic acid, at least in order of magnitude. For comparison the measured density (Fig. 6 of Cochran (1953)) has been re-drawn and is shown here as Fig. 4(*b*). The re-drawing consisted in changing the scale of the original (which represents a projection on a plane inclined to the molecular plane) so that the benzene ring appeared as a regular hexagon again, and then averaging densities over eight of the twelve areas that would be equivalent in benzene itself—the number being reduced to eight by the presence of substituent hydroxyl and carboxyl groups in salicylic acid. This procedure cannot be justified in detail, but serves to reduce the random errors of the original. When one remembers that the densities in Figs. 4(*a*) and 4(*b*) both represent differences between much larger densities (about 20 times larger, on the average), the agreement between them is seen to be quite good in the regions between bonded atoms. The fact that the densities at and near the centre of a carbon atom do not agree (measured, 0; calculated, $-0{\cdot}20$ e.Å^{-2}) is to be expected, since the measured difference density was used to find a scale factor and the temperature factors of the individual atoms, and at any stage of the refinement process (of which Fig. 6 of the 1953 paper is the final product) a density different from zero was corrected away by change of these factors. Only at the centre of the benzene ring is there a real discrepancy between Figs. 4(*a*) and 4(*b*), and the reasons for this are not known.

Figs. 5(*a*) and 5(*b*) show calculated and measured difference densities from which hydrogen atoms have not been subtracted, and thus make possible a comparison of calculated with measured electron densities in the projection of a bonded hydrogen atom—bonded to carbon, that is. Fig. 5(*b*) was obtained by redrawing Fig. 7 of the 1953 paper in the way described above. The agreement between Figs. 5(*a*) and 5(*b*) is reasonably close. It also follows from the low difference densities in the neighbourhood of the position of the hydrogen atom of Fig. 4(*a*) that the bonded atom closely resembles an isolated one in the (1*s*) state, as appears to be true in practice (McDonald, 1956). The point of maximum electron density of a hydrogen atom was found to be moved inwards from the nucleus by about 0·15 Å in the projection of salicylic acid, but this effect (if it is correct) is not explained by the calculated density of Fig. 5(*a*), which shows a displacement in the same direction, but of about 0·03 Å only.

Too much should not be made of any agreement in detail between Figs. 4(*a*) and 4(*b*) or between Figs. 5(*a*) and 5(*b*), as it may be fortuitous. The calculated density has been found by a comparatively crude method. The measured difference density depends on the temperature factors of the individual carbon and (to a lesser extent) hydrogen atoms, and these were not determined by any independent experiment. It also depends on the scattering factor of an unbonded carbon atom, and that used in the work on salicyclic acid had only an empirical basis. The calculation has served to emphasize the need for attention to these and other points in future work. It has however confirmed the rather surprising result that the formation of covalent bonds between atoms does not necessarily lead to any great departure from the 'unbonded' electron distribution for any of them, including hydrogen (see also McWeeny (1954)).

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