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Citation: *The Journal of Chemical Physics* **17**, 595 (1949); doi: 10.1063/1.1747343

View online: <http://dx.doi.org/10.1063/1.1747343>

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A Geometric Approach to the Theory of the Carbon-Carbon Bond*

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(Received July 23, 1948)

A geometric method of constructing the carbon-to-carbon bonds is described. It is postulated that there exists a region of high, constant electron density between the bound atoms. Calculations based on this postulate confirm it in that they lead to screening constants which are in fair agreement with the values given by Pauling and that plots of the variation of electron density with changes in the angular or radial variables reflect just such a region. Further, the plots are in good qualitative agreement with the well-known properties of rotation about a single bond and lack of rotation about a double bond.

IN a previous paper¹ a discussion was presented of the variation of electron density about tetrahedrally and trigonally hybridized carbon atoms. The treatment of directed valence there presented suggests the possibility of a simple and fruitful geometric approach to the problem of the chemical bond. In the present paper, only the commonest carbon-to-carbon bonds will be considered. Even these cases are simplified, perhaps idealistically, by regarding the possible other bonds which the carbon atoms may sustain as having no influence on the bond in question. Polarization effects in a bond will, of course, require corrective factors, whether these effects be due to adjacent bonds or to different electronegativities in the atoms joined. But such corrections will only serve to complicate the calculations; the essential features can best be presented without introducing those refinements.

To recapitulate briefly, the model upon which the reasoning is based is as follows: a sphere whose radius is arbitrarily taken as that at which a maximum electron density is attained. Upon the surface of this sphere, therefore, there are centers of maximum density whose relative location is determined by the state of "hybridization" of the hydrogen-like orbitals of the atom. For tetrahedral carbon, these centers are of equal density and are located at tetrahedral angles with respect to one another, while for trigonal carbon there are three centers of equal density located in a plane at intervals of 120° around the atomic core, plus two other centers of lesser density located within the sphere whose surface contains the first three and at right angles to the plane of those three. Upon moving away from these centers in any direction, the density will be found to diminish in accordance with the properties of the wave functions studied in the previous paper.

Now the concept that the formation of a bond re-

quires overlapping of orbitals from the participating atoms has long been well established.² Thus, it is considered that a chemical bond between two such atoms as have been described involves their mutual approach until their two electron clouds interact in such a way as to impart a maximum stability to the system. A very convenient and reasonable way to look at this is to consider the condition of maximum stability as obtaining when there exists in the region between the two atoms a space where the density of electrons is substantially constant. This space constitutes a region of electrical homogeneity. In order to break this bond and separate the two atoms, it will be necessary to disrupt this homogeneity—a process which will consume energy in an amount increasing with the extent of the disruption. The energy so consumed should closely correspond to the quantity which is termed the energy of the bond.

In a system in which polarization forces are either non-existent or equally balanced about a bond between two atoms, *A* and *B*, it is to be expected that along the axis between these atoms there should be an interval through which the summation of electron contributions of the two atoms will show a negligible variation. Two well-defined points within this interval may be picked, one being the midpoint, *a*, at which the radius is that measured experi-

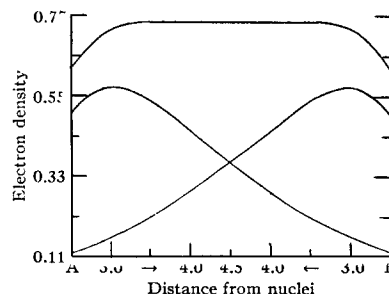


FIG. 1. Variation of electron densities with distances from atomic cores in an unpolarized bond between two tetrahedrally hybridized carbon atoms. Atomic units given are in terms of Zr/a_0 . The midpoint of the total *AB* abscissa represents the midpoint of the bond.

* This material is taken from a thesis presented by the author to the Graduate School of the University of Oregon in partial fulfillment of the requirements for the Ph.D. degree in chemistry.

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¹ H. K. Zimmerman, Jr. and P. Van Rysselberghe, *J. Chem. Phys.* **17**, 598 (1949).

² See for example S. Glasstone, *Theoretical Chemistry* (D. Van Nostrand Company, Inc., New York, 1944), pp. 107–12.

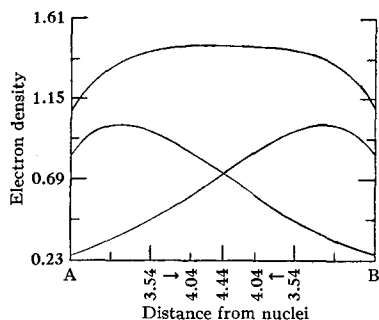


FIG. 2. Variation of electron densities with distances from atomic cores in an unpolarized bond between two trigonally hybridized carbon atoms. Atomic units are given in terms of Zr/a_0 . The midpoint of the total AB abscissa represents the midpoint of the bond.

mentally, and the other, b , being that at which the radius from one of the atomic cores, say A , is equal to the extremal value.¹ The distance of this second point from the core of atom B may then be easily expressed as a function of these two parameters. Then, making use of probability distribution functions,³ one may write

$$D_a = D_b, \quad (1)$$

where D_a is the density at point a (the sum of equal contributions from atoms A and B), and D_b is the density at point b (the sum of the contribution from atom A and a lesser contribution from atom B).

Thus, in the case of the bond between two tetrahedral carbon atoms,

$$D_a = D_{aA} + D_{aB} = 2D_{aA}, \quad (2)$$

where D_{aA} is the density at point a contributed by atom A , while that contributed by atom B is D_{aB} . Since the two contributions are equal at the midpoint between the two nuclei, the second equality is obvious. At point b , a similar expression may be

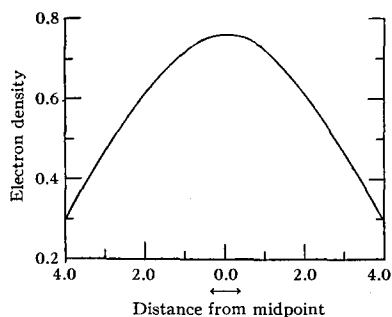


FIG. 3. Variation of electron densities with variation of the angle, θ_1 , keeping all other angles constant. Distances are measured along a line parallel to the z axis and passing through the midpoint of the internuclear axis, for the tetrahedral carbon-carbon bond. Atomic units given are in terms of Zr/a_0 .

³ L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 139.

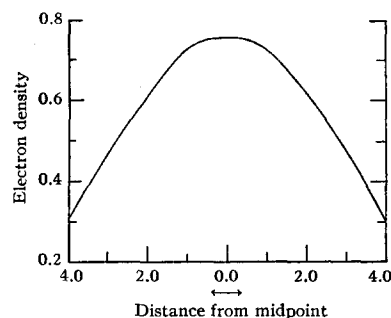


FIG. 4. Variation of electron densities with variation of the angle, ϕ_1 , keeping all other angles constant. Distances are measured along a line perpendicular to the z axis and to the internuclear axis, and passing through the midpoint of the internuclear axis, for the tetrahedral carbon-carbon bond. Atomic units given are in terms of Zr/a_0 .

written:

$$D_b = D_{bA} + D_{bB}, \quad (3)$$

where the notation is analogous. Here, however, the contributions of the two atoms, A and B , are unequal, so that we must retain the explicit sum.

In the case of the double bond (between two trigonal carbons) entirely analogous expressions may be written. It, must, however, be remembered that, for example,

$$D_{aA} = D_{aA_t} + D_{aA_p}, \quad (4)$$

wherein D_{aA_t} is the contribution of the trigonal orbital of atom A , and D_{aA_p} is that of the p_z orbital. Clearly, D_{aA_p} is zero along the internuclear axis because of the effect of the angular variable which it contains, but at any point above or below the plane of the trigonal orbitals, it makes a definite contribution which must be included.

All these densities may be readily expressed in terms of functions previously given,¹ it being remembered that the tetrahedral function to be considered is a four electron function, while the trigonal function is a three electron function. Thus, in order to have comparable single electron functions with which to work, we take the fourth root of our total tetrahedral function, $(\psi_{tet})^{\frac{1}{4}}$, and the cube root of our total trigonal function, $(\psi_{tri})^{\frac{1}{3}}$. In order to be entirely precise and general, the densities which we then obtain should be written as integrals of these single electron functions over the whole of the space encompassing the bond. But because of the great difficulty in evaluating such integrals, we have introduced the approximation of mapping only the probability distribution functions at a number of successive points. Thus, we write for the "density" at point a in the tetrahedral bond, the expression

$$D_a = 2D_{aA} = 2((\psi_{tet})^{\frac{1}{4}})^2, \quad (5)$$

and analogous expressions for D_b (tetrahedral) and D_a and D_b (trigonal).

In the expressions for the forementioned functions, there still occurs the undetermined parameter, Z , which is the effective positive charge on the core of the atom under consideration. Thus, the expansion of Eq. (1) for either the trigonal case or the tetrahedral one turns out to be a complicated expression in Z as the unknown. The solution of this expression is somewhat laborious, since the form of the equation requires that it be performed graphically; however, since the procedure is straightforward, space will not be consumed to present it in detail here. By this method, it has been calculated that, for tetrahedral and trigonal carbon, respectively,

$$Z = 3.09, \quad (6)$$

$$Z = 3.50. \quad (7)$$

These values correspond respectively to screening constants of 0.3 and 0.25 for the electrons in the "hybridized" systems. They are thus in fair agreement with the approximate screening constant of 0.4 electron units given by Pauling⁴ and so tend to confirm the correctness of the reasoning.

Employing the values for Z just given, it is now possible to calculate numerical values for the sums of probability distribution functions (expressed by Eqs. (2) and (3) and their analogs) in the bond between two unpolarized tetrahedral carbon atoms and between two unpolarized carbon atoms in the sort of double bond first suggested by Hückel,⁵ at any desired radius along the internuclear axis. Such values have been calculated at a number of points, and it is found that they follow curves like those shown in Fig. 1 for the tetrahedral bond and in Fig. 2 for the double bond. In each of these figures, the two lower curves are radial variations of the probability distribution functions (i.e., electron density number) for the separate atoms, while the upper curve represents the summation of the two contributions to electron density. The manner in

which the nearly linear portions of the curves from the individual atoms combine to give a high, constant density over a very considerable range furnishes a striking confirmation of the original hypothesis.

The confirmation is strengthened if one examines the effect of a variation in one or another of the angular coordinates of each of the atoms in the bond. In Figs. 3 and 4 there are shown, respectively, the summed densities obtained by varying θ_1 and ϕ_1 about the extremal values previously given,¹ during each variation keeping all other angular parameters constant at the extremal values. The axis on which the sums are taken is a line perpendicular to the internuclear axis. Thus, in Fig. 3, the variation may be considered to be along a line parallel to the p_z axis of maximum density. At large variation of θ_1 from its maximum value, the density of electrons is seen to be relatively low. But as the maximum value is approached, this density on the line chosen for consideration increases continually until at last it is seen that there is a fairly considerable region of high and constant density in the neighborhood of the midpoint on the internuclear axis (i.e., the maximum value of θ_1). Similarly, in Fig. 4, the variation is along a line in the x, y plane and perpendicular to the internuclear axis. The variation in density with changes in ϕ_1 is then seen to behave in just the same way as it does with the changes in θ_1 . The results of parallel calculations for the Hückel double bond are presented in Figs. 5 and 6 and are also seen to be in agreement with the hypothesis.

A further interesting result may be observed in the matter of the angular symmetry reflected by Figs. 3 and 4, wherein the curves are virtually identical even though the planes of the angular coordinates being varied are mutually perpendicular, in contrast to the obvious lack of such symmetry shown by Figs. 5 and 6, wherein variations on the mutually perpendicular planes of the angular coordinates lead to very different curves. Thus it appears that a rotation of 90° in one atom with respect to the other involves no alteration of electron density

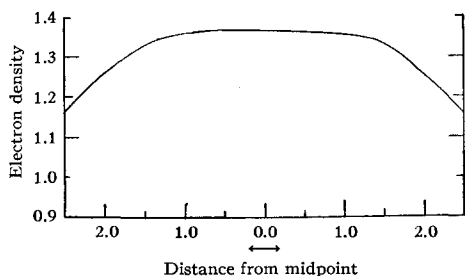


FIG. 5. Variation of electron densities with variation for the Hückel double bond of the angle, θ_1 , keeping all other angles constant. Distances are measured along a line parallel to the z axis and passing through the midpoint of the internuclear axis. Atomic units given are in terms of Zr/a_0 .

⁴ L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1944), p. 65.

⁵ E. Hückel, *Zeits. f. Physik.* 60, 423 (1930).

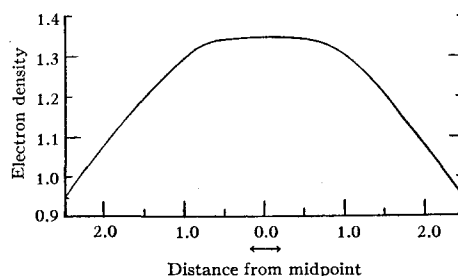


FIG. 6. Variation of electron densities with variation for the Hückel double bond of the angle, ϕ_1 , keeping all other angles constant. Distances are measured along a line perpendicular to the z axis and to the internuclear axis, and passing through the midpoint of the internuclear axis. Atomic units given are in terms of Zr/a_0 .

within the tetrahedral bond, while such a rotation requires a very substantial alteration of electron density within the double bond. The symmetry shown for the tetrahedral bond is therefore in agreement with the physical fact that there exists freedom of rotation about such a bond; every angular orientation achieved by rotating on the internuclear axis is identical in electron density with every other, and as a consequence no expenditure of energy is needed to accomplish rotation. This, of course, does not consider steric hindrance to rotation which may arise through the potential fields of substituents on the two carbon atoms. In the double bond, on the other hand, Figs. 5 and 6 illustrate a marked lack of symmetry. Thus, any

rotation about that bond will require an alteration of the electron distribution and so an expenditure of energy which will make such a rotation very difficult to achieve. This, too, is in agreement with the well-known fact that rotation about a double bond is never accomplished except by the most extraordinary means.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor Pierre Van Rysselberghe whose criticism and counsel have made this study possible, and to the American Chemical Society under whose grant of a pre-doctoral fellowship it was performed.

Directed Valence as a Property of Determinant Wave Functions*

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(Received July 23, 1948)

Making use of Slater's extension of the Heitler-London method, it is shown that the directional properties of carbon valences are a logical consequence of the combination of the hydrogen-like individual electron orbitals of carbon into a determinant wave function. It is possible to separate the radial and angular parts of such a function by factoring. Partial differentiation of the factored function with respect to the angular variables leads to proof of the directional properties, while partial differentiation with respect to the radial variable shows that, as long as all valence electrons are at equal distances from the nucleus, the electron density is maximum at points located on a sphere whose radius is calculated.

FOR many years, Pauling's theory of directed valence¹ has been used with much success. However, his derivations require the use of certain postulated rules, the construction of successive linear combinations of one-electron wave functions (the first of which in the case of the carbon valences is assumed to contain contributions from only two of the four one-electron functions), the complete neglect of the influence of radial factors, etc. While these points do not invalidate the results of the calculations, they do tend somewhat to obscure the fundamental nature of the directed valence concept. Recently, there was published a paper² in which it is shown that the phenomenon of directed valence can be proved without the necessity of such assumptions. At the time this paper appeared, we were engaged in a calculation which parallels it, and since the mathematical equipment which we have chosen

is considerably simpler than the vector notation used by Artmann, it is considered that the treatment which is presented hereinafter represents an improvement over his derivation. In addition to this simplification in the mathematics, we have been able to show explicitly that radial factors need not be neglected in the present procedure and that they do not, in fact, influence the directional properties of the valences.

Since Artmann has already discussed numerous examples, we shall restrict ourselves mainly to the cases presented by tetrahedral carbon and by carbon as it occurs in the double bond. However, in order to make completely clear the principles of the method, we shall first consider the simplest possible case—that of the configuration, $p_x p_y$, as for example it occurs in the 3P state of oxygen. Employing the Slater extension of the Heitler-London method,³ the system of the two unpaired electrons may be written as the determinant,

$$\psi = \eta \begin{vmatrix} p_{x1} & p_{x2} \\ p_{y1} & p_{y2} \end{vmatrix} \quad (1)$$

* From a thesis presented by H. K. Zimmerman, Jr. to the Graduate School of the University of Oregon in partial fulfillment of the requirements for the Ph.D. degree in chemistry.

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¹ L. Pauling, *J. Am. Chem. Soc.* **53**, 1367-1400 (1931).

² K. Artmann, *Zeits. f. Naturfor.* **1**, 426-32 (1946).

³ J. C. Slater, *Phys. Rev.* **38**, 1109 (1931).