Directed Valence as a Property of Determinant Wave Functions

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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.

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Directed Valence as a Property of Determinant Wave Functions*

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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 valence[1] 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 paper[2] 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,

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

[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).

in which ψ is the wave function for the composite system, η is the normalization factor required by the combination of one-electron wave functions as a two-electron determinant wave function (*vide* infra), while p_x and p_y are the normalized one-electron hydrogen-like wave functions corresponding respectively to the sets of quantum numbers $n=2$, $l=1$, $m=1$ and $n=2$, $l=1$, $m=-1$, the subscripts 1 and 2 referring to the coordinates of the two electrons. The spins of the two electrons are taken parallel to each other. By substituting into Eq. (1) the explicit hydrogen-like wave functions and factoring out of the determinant the constants and radial factors (corresponding to equal values of the distances from the electrons to the center of the nucleus), one arrives at the expression,

$$\psi = \eta \left(\frac{1}{4(2\pi)^{\frac{1}{2}}} \right)^2$$

$$\times \left(\frac{Z}{a_0} \right)^3 \rho^2 \exp\rho \begin{vmatrix} \sin\theta_1\cos\phi_1 & \sin\theta_2\cos\phi_2 \\ \sin\theta_1\sin\phi_1 & \sin\theta_2\sin\phi_2 \end{vmatrix}, \quad (2)$$

where Z is the effective atomic number of the atomic core; a_0 is the radius of the first Bohr orbit, 0.529 angstrom and ρ, θ_2, θ_1, ϕ_2, and ϕ_1 are the spherical polar coordinates of the respective electrons, with

$$\rho = Zr/a_0, \quad (2a)$$

r being the actual radial coordinate in angstroms.

In order to establish the values of θ_1, θ_2, ϕ_1, and ϕ_2 at which ψ is an extremum, one now calculates the partial derivatives of ψ with respect to the θ's and ϕ's, equating each derivative to zero. This procedure leads to the system of four equations,

$$\left. \begin{aligned} \frac{\partial\psi}{\partial\theta_1} &= \begin{vmatrix} \cos\theta_1\cos\phi_1 & \sin\theta_2\cos\phi_2 \\ \cos\theta_1\sin\phi_1 & \sin\theta_2\sin\phi_2 \end{vmatrix} = 0 \\[6pt] \frac{\partial\psi}{\partial\phi_1} &= \begin{vmatrix} -\sin\theta_1\sin\phi_1 & \sin\theta_2\cos\phi_2 \\ \sin\theta_1\cos\phi_1 & \sin\theta_2\sin\phi_2 \end{vmatrix} = 0 \\[6pt] \frac{\partial\psi}{\partial\theta_2} &= \begin{vmatrix} \sin\theta_1\cos\phi_1 & \cos\theta_2\cos\phi_2 \\ \sin\theta_1\sin\phi_1 & \cos\theta_2\sin\phi_2 \end{vmatrix} = 0 \\[6pt] \frac{\partial\psi}{\partial\phi_2} &= \begin{vmatrix} \sin\theta_1\cos\phi_1 & -\sin\theta_2\sin\phi_2 \\ \sin\theta_1\sin\phi_1 & \sin\theta_2\cos\phi_2 \end{vmatrix} = 0 \end{aligned} \right\} \quad (3)$$

The solution of this system leads to the result that ψ is an extremum[4] when the angular coordinates of the two electrons are such as to give a bond angle of 90°. However, while the condition involving the first partials is a necessary condition which must be satisfied to show existence of an extremum, it is not

necessarily sufficient. In order to have unequivoca-proof, it should, if possible, be shown that the del terminant of all second partials of ψ is not zero. Thus, using the general notation, κ, for all the angular variables,

$$\left| \frac{\partial^2\psi}{\partial\kappa_n\partial\kappa_m} \right| > 0 \qquad \begin{aligned} n &= 1, 2, 3, 4, \\ m &= 1, 2, 3, 4, \end{aligned}$$

indicates the angular values calculated give a minimum, while

$$\left| \frac{\partial^2\psi}{\partial\kappa_n\partial\kappa_m} \right| < 0 \qquad \begin{aligned} n &= 1, 2, 3, 4, \\ m &= 1, 2, 3, 4, \end{aligned}$$

indicates that they give a maximum. If we take as the solution of the system of equations, (3), the values,

$$\begin{aligned} \theta_1 &= 90° & \phi_1 &= 0° \\ \theta_2 &= 90° & \phi_2 &= 90°; \end{aligned} \quad (4)$$

however, it is found that the determinant is identically zero. Therefore, it is necessary to fall back upon a less satisfactory method of trial and error to show that the results, (4), give an extremum. This can be done by introducing a small variation into one of the angular values which have been calculated, while keeping the other values as previously found. When this is done and the value of the determinant in Eq. (2) calculated for a number of such variations, it is found that all these result in a lower value of the determinant than is found with the values, (4). Hence, it may reasonably be concluded that the values given do actually result in a maximum.

A further way in which the same result may be shown is the following.[†] In the present simple example, the determinant of Eq. (2) may be readily expanded to the form

$$\psi = F(\rho)(\sin\theta_1\cos\phi_1\sin\theta_2\sin\phi_2$$
$$- \sin\theta_1\sin\phi_1\sin\theta_2\cos\phi_2).$$

This is identically equal to

$$\psi = F(\rho)(\sin\theta_1\sin\theta_2\sin(\phi_2-\phi_1)).$$

It is therefore obvious that the maximum value of the angular function occurs for the angles given in (4). Thus one is able immediately to see that the function actually depends only on the three variables, θ_1, θ_2, $(\phi_2-\phi_1)$; i.e., ϕ_1 and ϕ_2 are not independent of each other, and the function is maximum for $\theta_1 = \theta_2 = \phi_2 - \phi_1 = 90°$.

Considering now the tetrahedral carbon atom, we apply the Slater extension of the Heitler-London method to the ^5S state into which the carbon atom

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[4] Cf. H. Hancock, *Theory of Maxima and Minima* (Ginn and Company, Boston, 1917), pp. 79–82.

[†] This point was indicated by the reviewer of this article, to whom the authors wish to express their thanks.

may be considered to have been thrown by the process of approaching chemical combination. Hence, we have the composite system as the determinant,

$$\psi_{\text{tet}} = \eta^{\frac{1}{3}} \begin{vmatrix} s_1 & s_2 & s_3 & s_4 \\ p_{x1} & p_{x2} & p_{x3} & p_{x4} \\ p_{y1} & p_{y2} & p_{y3} & p_{y4} \\ p_{z1} & p_{z2} & p_{z3} & p_{z4} \end{vmatrix} \quad (5)$$

in which η is again a normalizing factor.[5] It should be noted that such a determinant as (5) is the only way of building a four electron wave function which is antisymmetrical with respect to each of the four electrons: permutation of any two columns changes the sign of the function.

Substituting into Eq. (5) the expressions for the hydrogen-like wave functions, and factoring out the constants and radial factors (corresponding again to equal values of the distances of the four electrons from the center of the nucleus),

$$\psi_{\text{tet}} = \eta^{\frac{1}{3}}(1/4(2\pi)^{\frac{1}{3}})^4(Z/a_0)^6\rho^3(2-\rho)\exp(-2\rho)$$

$$\times \begin{vmatrix} 1 & 1 & 1 & 1 \\ \sin\theta_1\cos\phi_1 & \sin\theta_2\cos\phi_2 & \sin\theta_3\cos\phi_3 & \sin\theta_4\cos\phi_4 \\ \sin\theta_1\sin\phi_1 & \sin\theta_2\sin\phi_2 & \sin\theta_3\sin\phi_3 & \sin\theta_4\sin\phi_4 \\ \cos\theta_1 & \cos\theta_2 & \cos\theta_3 & \cos\theta_4 \end{vmatrix} \quad (6)$$

The special case, $\rho_1 = \rho_2 = \rho_3 = \rho_4 = \rho$, makes the study of the angular behavior of the function, ψ_{tet}, particularly convenient. The experimental equivalence of the four carbon bonds, as in methane, for instance, indicates that the four ρ's have equal time averages and provides a justification for our procedure.

It is now necessary to determine the values of the θ's and ϕ's which simultaneously cause the partial derivatives of ψ_{tet} with respect to each of the eight angular variables to vanish. These values will then include those of the eight variables which make the function an extremum.[4] Thus, again using the

general notation, κ_n, to denote the θ_n and ϕ_n, our problem is to calculate the partials, $\partial\psi_{\text{tet}}/\partial\kappa_n$, and to equate them to zero. Here, even more than in the preceding simple example, the operation is substantially simplified because of the fact that the particular angles, κ_n, are all in a single column of the determinant. Thus, for instance, the expression for the partial derivative of ψ_{tet}, as given in Eq. (6), with respect to θ_1 can be equated to zero as follows:

$$0 = \eta^{\frac{1}{3}}(1/4(2\pi)^{\frac{1}{3}})^4(Z/a_0)^6\rho^3(2-\rho)\exp(-2\rho)$$

$$\times \begin{vmatrix} 0 & 1 & 1 & 1 \\ \cos\theta_1\cos\phi_1 & \sin\theta_2\cos\phi_2 & \sin\theta_3\cos\phi_3 & \sin\theta_4\cos\phi_4 \\ \cos\theta_1\sin\phi_1 & \sin\theta_2\sin\phi_2 & \sin\theta_3\sin\phi_3 & \sin\theta_4\sin\phi_4 \\ -\sin\theta_1 & \cos\theta_2 & \cos\theta_3 & \cos\theta_4 \end{vmatrix} \cdot \quad (7)$$

Thus it is seen that the mathematical process of differentiating the composite wave function to determine its extremal angles, although a formidable task were the function an arbitrary sum-and-product relation of the eight angular variables, is very greatly facilitated by the use of the determinant. Hence, the determinant not only affords a convenient method of mathematically expressing the interchangeability of the electrons of the composite system, but it also makes possible an easy and straightforward analysis of the problem once it is stated by means of Eqs. (5) and (6).

This procedure yields a set of eight simultaneous equations in eight unknowns. In principle, the set might be solved analytically to give the eight extremal values of the θ's and ϕ's. However, such a procedure is an extremely complex undertaking, and it has been found more feasible to assume certain sets of values for these variables, testing them in the set of eight equations to determine whether they satisfy the system. In this manner, it is found that a set of variables describing four functions at tetrahedral angles with respect to one another does indeed satisfy the condition imposed. Numerically, these may be taken as follows:

$$\begin{array}{ll} \theta_1 = 54°\ 44' & \phi_1 = 0 \\ \theta_2 = 125°\ 16' & \phi_2 = \pi/2 \\ \theta_3 = 54°\ 44' & \phi_3 = \pi \\ \theta_4 = 125°\ 16' & \phi_4 = 3\pi/2. \end{array} \quad (8)$$

One can readily verify that twice 54° 44' is 109° 28', i.e., the tetrahedral angle. Also, 125° 16' is the difference between 180° and 54° 44', and thus the positions thereby selected for the four tetrahedral directions are obvious. The important point which the theory shows is that the condition of mutual tetrahedral orientation gives an extremum. This important circumstance is not immediately obvious from Eq. (5), since an expression of the form of (1) or (5) is actually invariant with respect to rotation of the coordinate axes.

Now the condition stated above is a necessary

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[5] In our actual calculations, we have normalized the function to four—unity for each electron in the system. Such a normalization expresses the fact that the total charge of the distribution represented by the four-electron function is that of four electrons. This type of normalization is useful when comparisons are to be made between functions involving different numbers of electrons, as will be the case later in the present paper. Further, when such composite functions are employed, as will be done in a subsequent paper, in the discussion of electron distributions in bonds, it is easy to show that, as a matter of fact, the normalization to four is very little different, in its influence on the numerical values obtained, from the more usual normalization to unity. Although it is not a complete or accurate way of treating the problem, normalization to four here is, in effect, simply a way of taking into account the repulsion of a given electron in the system by the other three, i.e., the density of distribution is somewhat greater in the bond direction with this normalization to four than with the normalization to unity. However, since this step does not affect the present demonstration of the angular properties, it may, if desired, be regarded merely as an arbitrary constant for the purpose of this paper. Similar remarks, with a normalization to three, also apply to the trigonal system discussed later in this paper.

requirement for an extremum. Its sufficiency in this case is demonstrated by the fact that the determinant of all second partials of ψ_{tet} is negative. Thus,

$$\left| \frac{\partial^2 \psi}{\partial \kappa_n \partial \kappa_m} \right| < 0 \qquad \begin{array}{l} n = 1, 2, \cdots, 8 \\ m = 1, 2, \cdots, 8 \end{array}$$

In the case of the double bond, the theory first proposed by Hückel[6] states that this bond consists of two parts: a secondary portion which consists of unhybridized $2p_z$ orbitals, and a primary portion which consists of a hybrid of the remaining three hydrogen-like orbitals of the outer shell of the carbon atom. This hybrid corresponds to what is often designated as "trigonal quantization." It gives the directional properties to the bond. In the same manner as before, this "hybrid" can be formulated as a composite function in the following way:

$$\psi_{tri} = \eta^{\frac{1}{2}} (1/4(2\pi)^{\frac{1}{2}})^3 (Z/a_0)^{9/2} \rho^2 (2-\rho) \exp(-3\rho/2)$$

$$\times \begin{vmatrix} 1 & 1 & 1 \\ \sin\theta_1 \cos\phi_1 & \sin\theta_2 \cos\phi_2 & \sin\theta_3 \cos\phi_3 \\ \sin\theta_1 \sin\phi_1 & \sin\theta_2 \sin\phi_2 & \sin\theta_3 \sin\phi_3 \end{vmatrix}, \quad (9)$$

in which η is once more a normalizing factor.[5]

Determination of the parameters, θ_n and ϕ_n, follows the same pattern as before, one set of values which simultaneously set the six first partial derivatives equal to zero being found to be

$$\begin{array}{ll} \theta_1 = \pi/2 & \phi_1 = 0 \\ \theta_2 = \pi/2 & \phi_2 = 2\pi/3. \qquad (10) \\ \theta_3 = \pi/2 & \phi_3 = 4\pi/3 \end{array}$$

However, as in the first case presented in this paper, calculation of the value of the determinant of second partial derivatives yields zero. But by introducing a moderate variation into the values of θ_1 and ϕ_1, meanwhile keeping all the other values at the figures given in (10), the value of the determinant can be calculated for a number of cases. Such calculations have shown that all such cases give values lower than that found from the combination, (10). This may be taken as presumptive evidence that the angles do determine a maximum.

Moreover, as in the case of ^3P oxygen discussed above,† the determinant of Eq. (9) may be expanded, and the appropriate identities used, to obtain the expression

$$\psi_{tri} = (\sin\theta_1 \sin\theta_2 \sin(\phi_2 - \phi_1) + \sin\theta_2 \sin\theta_3 \sin(\phi_3 - \phi_2) + \sin\theta_3 \sin\theta_1 \sin(\phi_1 - \phi_3)) f(\rho).$$

From this it is again clear that the function is maximum when the θ's are all 90°, the foregoing

⁶ E. Hückel, Zeits. f. Physik. **60**, 423 (1930).

expression then reducing to

$$\psi_{tri} = (\sin x + \sin y - \sin(x+y)) f(\rho),$$

where

$$\begin{array}{l} x = \phi_2 - \phi_1, \\ y = \phi_3 - \phi_2. \end{array}$$

Thus it is once again apparent that, since only the differences of the ϕ's are significant, the number of independent variables among the ϕ's is once more reduced by one. This circumstance serves to indicate the reason for the difficulty encountered in showing the existence of extrema in two of the three cases studied, by the use of determinants only. However, the determinant treatment has been preserved throughout because of the advantages which it offers in the more complex cases, of which the tetrahedral is an example.

This last case presents, perhaps more forcibly than does that of the tetrahedral carbon, the distinction between the angular invariance of the composite wave functions and the fact—which is of such great importance chemically—that the angle between any given pair of "hybridized" valences possesses an optimum value which causes the composite function to assume a maximum value.

From an inspection of the form of Eqs. (6) and (9), it becomes apparent that the positions of the angular extrema determined through the method of partial derivatives are unaffected by the radial factors so long as those factors are the same for each of the four electrons and so can be factored. If now the angular variables are held constant, Eq. (6) may be written as

$$\psi_{tet} = K(Z/a_0)^6 \rho_{tet}^3 (2-\rho_{tet}) \exp(-2\rho_{tet}), \quad (11)$$

and Eq. (9) may be written as

$$\psi_{tri} = k(Z/a_0)^{9/2} \rho_{tri}^2 (2-\rho_{tri}) \exp(-3\rho_{tri}/2). \quad (12)$$

Now, in general the differential element of the electron distribution about the atomic core corresponding to the "hybrid" function, ψ, may be written as

$$\psi^2 \prod_1^n \rho_n^2 d\rho_n ds_n \qquad (13)$$

in which each differential ds_n is an element of surface area on the unit sphere.

In order to make use of the angular extrema calculated above, we shall restrict ourselves to a consideration of small elements of solid angle, which are defined by the ds_n, in the extremal directions. In order to give physical meaning to the concept of distribution in such an element, it is necessary that the element be of a constant angular opening. Thus, within the limits of the physical model which we are considering, the four factors, ds_n, are equal to one another and constant. This has the effect of fixing

the size of the solid angle with which we are dealing in any particular direction.

Since it has been seen that the angular extrema are unaffected by the radial factors for a function of the type of Eq. (6) and Eq. (9), it is reasonable to expect that the inverse statement also is true. Hence, let us hold all the angular factors in expression (13) equal to some constant value (say an extremal value) for the present. This places us within the confines of some element of solid angle. Further, we shall set all the $d\rho_n$ constant, in effect prescribing thereby the depth of the four volume elements whose product is given by (13). The precise value given to $d\rho_n$ need not concern us. The size of these volume elements will now vary with ρ^2 only. The radial distribution functions are then given by the expressions,

$$K'\rho_{tet}^{14}(2-\rho_{tet})^2 \exp(-4\rho_{tet}) \qquad (14)$$

for the tetrahedral system, and

$$k'\rho_{tri}^{10}(2-\rho_{tri})^2 \exp(-3\rho_{tri}) \qquad (15)$$

for the trigonal hybrid. In order to find the respective ρ which make these distribution functions maximum, we then take the derivatives of (14) and (15) with respect to their ρ, set each of these derivatives equal to zero, and solve for ρ. The extremal values of ρ found by this procedure are

$$\rho_{tet} = 4.414, \qquad (16)$$

$$\rho_{tri} = 4.53. \qquad (17)$$

It is interesting to note that these values are nearly equal to each other. The actual values of $(\psi_{tet})^{\frac{1}{4}}$ and $(\psi_{tri})^{\frac{1}{3}}$ at the ρ's, θ's and ϕ's giving extrema should be similar for justification of normalization[5] to four and three.

It might be pointed out that, whenever the ρ's of the various electrons are taken equal to one another, the complete four- or three-electron wave function is maximum for the values of ρ_{tet} and ρ_{tri} given by (16) and (17) regardless of the values chosen for the angular variables. In other words, regardless of the values given to the angles, the wave function is maximum for those angles when the four or three electrons are on the sphere corresponding to $\rho_{tet} = 4.414$ or $\rho_{tri} = 4.53$, the maximum of all these maxima occurring for the tetrahedral or trigonal configuration.

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The Formula of Uranyl Ion*

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The exchange of oxygen between uranyl ion and water was studied using oxygen 18 as a tracer. The results showed that the formula of uranyl ion in dilute hydrochloric acid solution is UO_2^{++}, neglecting any anion complexing, as distinguished from $U(OH)_4^{++}$, unless in $U(OH)_4^{++}$ two of the oxygen atoms are much more weakly bonded than the other two. The UO_2^{++} ion is covalently bonded in dilute hydrochloric acid solution as well as in crystalline uranyl chloride. The Raman spectrum of uranyl perchlorate was measured and the available Raman spectra of uranyl salts are interpreted considering the effects of complex ion formation.

FOR some time it has been generally assumed that uranyl ion is a doubly positive charged ion in acid solution. Freezing point studies[1] of uranyl

chloride and uranyl nitrate have shown that they behave as completely dissociated ternary electrolytes. Isopiestic vapor pressure measurements[2] have shown that uranyl nitrate is a completely dissociated 1–2 electrolyte. Best, Taub, and Longsworth[3] measured the pH of uranyl chloride solutions up to 0.5 M concentration and found that very little

1 C. Dittrich, Zeits. f. physik. Chemie 29, 449 (1899).

2 R. A. Robinson, J. W. Wilson, and H. S. Ayling, J. Am. Chem. Soc. 64, 1469 (1942).
3 R. J. Best, D. Taub, and L. G. Longsworth, Manhattan District Report CCA 380 (Nov. 1942).