in the spectra of the trideuterated compound, but it is believed that 160 cm.$^{-1}$ is close to where ν_{18} could be found. The final assignment is shown in Table I.

To obtain a final check on the assignment of the fundamentals of the normal and trideuterated compound, the ratios for the product rule were calculated for both species A$'$ and A$''$. The moments of inertia around the three principal axes needed for this computation were obtained from the microwave data.[3] The values are in atomic mass units times Å.^{2}

$$I_A = 9.633 \quad I_B = 47.389 \quad I_C = 53.831$$

$$I_A = 12.795 \quad I_B = 55.613 \quad I_C = 62.031$$

for normal and trideuterated amine, respectively.

The computed values of the product rule are 0.203 and 0.323 for species A$'$ and A$''$. The corresponding values obtained from the frequencies observed are 0.227 and 0.346 for the matrix spectra and for the pure solid 0.215 and 0.321, respectively. The agreement, especially for the solid is quite good, indicating that there are no gross inconsistencies in the assignment. The somewhat high values for the matrix spectra are attributed to the fact that, in the case of the spectrum of the deuterated species in the matrix, the amine concentration must have been high. This is reflected also in the broader lines observed in this spectrum.

Binding Regions in Polyatomic Molecules and Electron Density Distributions

BY R. F. W. BADER[1]

The concept of a binding region as developed by Berlin[2] is extended to polyatomic molecules. Various electron density distributions for the water molecule are examined to determine whether or not they concentrate charge density in the binding region, a necessary requirement for the attainment of electrostatic equilibrium. This is accomplished by plotting the difference in density ($\Delta\rho$) between a proposed molecular density distribution and one obtained from the original atomic densities located with the same molecular geometry. The latter distribution does not concentrate sufficient charge density in the binding region to balance the nuclear forces of repulsion, and thus the sign of $\Delta\rho$ in the binding region provides a test of proposed density distributions. In this manner, limits may be placed on the form of an acceptable density distribution for the water molecule. It is found that the lone-pair orbitals must possess close to sp hybridization and that the bonds to the hydrogen atoms must be "bent" and of almost pure 2p character. It is also shown that the lone-pair density plays an essential role in binding the protons in the water molecule.

In 1950 Berlin[2] introduced the valuable concept of dividing the space in a homonuclear diatomic molecule into binding and antibinding regions. Electron density placed in the region between the two nuclei (the binding region) exerts forces on the nuclei drawing them together, while electron density placed behind either nucleus (the antibinding region) exerts unequal forces on the nuclei and leads to the separation of the molecule into atoms. These two spatial regions are separated by two surfaces (see Fig. 1a) which pass through the nuclei and which have the property that any negative charge density placed on these surfaces exerts an equal force along the bond axis on both nuclei. These boundary curves thus represent positions from which electron density neither increases nor decreases the internuclear distance. It is worth stressing that the concept of a binding region is a rigorous one, being a direct result of the Hellmann–Feynman[3] theorem. This theorem states that the force on any nucleus in a molecule is the sum of the electrostatic forces due to the other nuclei and to the electron charge distribution treated as a continuous charge density by classical methods.

Charge density must be concentrated in the binding region to achieve electrostatic equilibrium. Thus a knowledge of the binding region for a polyatomic molecule would be useful in that various charge distributions could be tested to determine whether or not

they do indeed concentrate charge density in this region. The backbone of the density distribution for a molecule composed of atoms from the first two periods will be in terms of the 1s orbital for the hydrogen atom, and the 1s, 2s, and 2p orbitals for the other atoms present. Since so much of the chemist's reasoning and theories of electronic structure are couched in terms of the 1s, 2s, and 2p orbitals, it is important to know the limiting forms of the best possible description of a density in terms of these orbitals. It is the purpose of the present method to provide these limiting density distributions.

To construct the binding region for the water molecule, which we choose to illustrate the procedure, we first consider the case of a heteronuclear diatomic molecule. There will be a point on the internuclear axis at a distance r behind the nucleus of smaller charge at which an element of negative charge density will exert equal forces on both nuclei, i.e., $Z_A/(R + r)^2 = Z_B/r^2$ for some value of r when $Z_A > Z_B$ and R is the bond length. This is illustrated in Fig. 1b. Thus for a heteronuclear diatomic molecule, one boundary surface curls back onto itself to form an enclosed region, while the boundary surface through the nucleus of greater charge opens up and approaches a straight line perpendicular to the bond axis. This has been pointed out by Hirschfelder, et al., who also give the equations for the boundary curves.[4] For an O–H

(1) A. P. Sloan Research Fellow.
(2) T. Berlin, J. Chem. Phys., 19, 214 (1951).
(3) R. P. Feynman, Phys. Rev., 56, 340 (1939).

(4) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954. p. 935.
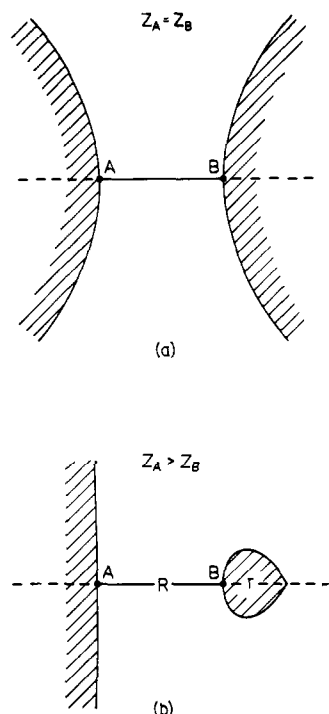
Fig. 1.—(a) Binding and antibinding regions in a homonuclear diatomic molecule (antibinding region is shaded);   (b) binding and antibinding regions in an O–H molecule.

bond r is approximately one-half of the bond length. We can construct a binding region for the water molecule by superimposing two such O–H diagrams inclined at the bond angle with a common oxygen nucleus. Doing this we obtain an angularly shaped binding region enclosed within the geometry of the molecule as illustrated in Fig. 2. This region is determined entirely by the two boundary curves through the oxygen nucleus as the antibinding regions in the vicinities of the protons (including those generated by considering the diatomic group H–H) lie entirely outside of this binding region. The angle immediately subtended at the oxygen nucleus by the two boundary curves is $\varepsilon - 2(\varepsilon - 90°) = 76°$ when $\varepsilon = 104.45°$.[5] The boundary curves have the following significance. Any negative charge density placed inside this region simultaneously attracts all three nuclei and thus binds the molecule. Any charge density placed outside of this region exerts forces on the nuclei such as to increase at least one of the internuclear distances, i.e., charge in other regions results in forces which would lead to the formation of a diatomic molecule and an atom. Charge density on either of the boundary curves exerts an equal force on the oxygen nucleus and one of the hydrogen nuclei along one bond and a force tending to decrease the internuclear distance between the oxygen and the second hydrogen. Any charge density in the perpendicular plane of the molecule exerts equal forces on the protons along the O–H bonds. Thus a single, almost horizontal line divides the binding from the antibinding region in the plane perpendicular to the molecular plane. This is illustrated in Fig. 3. Any charge density below this line simultaneously exerts binding forces on all three nuclei.

(5) L. Sutton, Special Publication No. 11, The Chemical Society, London 1958.
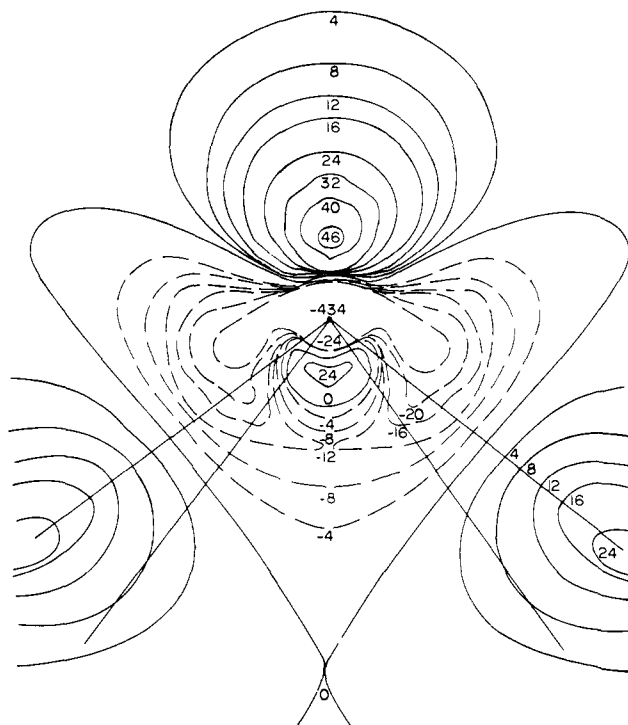

Fig. 2.—Plot of $\Delta\rho$ for density distribution I in the molecular plane. The hydrogen nuclei are located at the ends of the two lines subtending the largest angle at the oxygen nucleus. The two inner lines are the boundaries dividing the binding and antibinding regions. The $\Delta\rho$ values are in atomic units $\times$ 100 $[(e/a_0{}^3) \times 100]$.
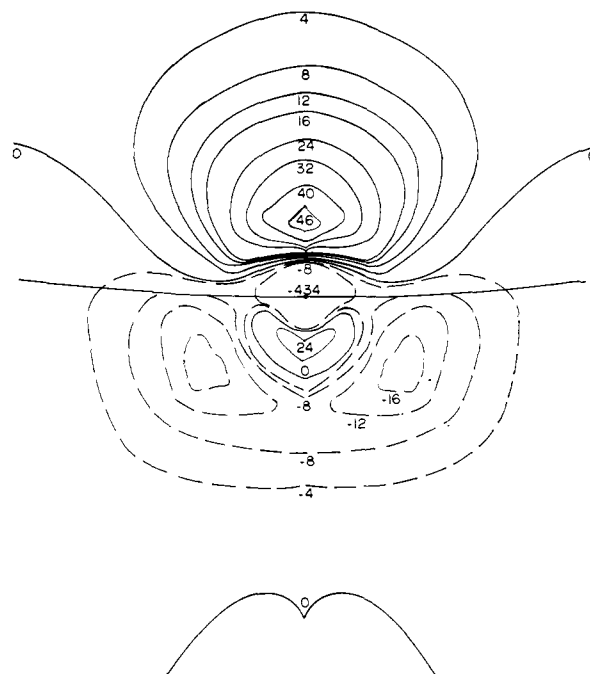

Fig. 3.—Plot of $\Delta\rho$ for density distribution I in the perpendicular plane. All the figures are plotted to the same scale. The nearly horizontal line divides the binding region (lower half) from the antibinding region.

It is interesting to note that as the bond angle ε decreases, the angle subtended by the binding region boundaries and the area of the binding region itself increases. For example, in H_2S, where the bond angle is 92.2°,[5] the angle of the boundary curves has increased to 87.8°. Hydrides of the third-row elements, e.g., H_2S and PH_3, invariably possess bond angles

smaller than their analogs in the second period, H_2O and NH_3. Since the density employed in binding the protons in the third-period elements is more diffuse and further from the heavy nucleus than in the second-row elements, the decrease in the bond angle can be correlated with the increased area of the binding region thus obtained.

The density distribution for any state of the water molecule must possess the same symmetry as that of the nuclear framework. Thus, for any element of charge density in the molecular plane to one side of the symmetry axis, there will be a corresponding symmetrically placed element. One can construct a new boundary curve in the molecular plane dividing the binding and antibinding regions by considering the forces exerted on the nuclei by such pairs of symmetrically related charge elements. This results in a more extended binding region. The boundary curve through the oxygen nucleus is very similar to the curve for the perpendicular plane, since the hydrogens are now equivalent with respect to the pair of density elements. In addition, a small enclosed region behind each hydrogen nucleus is also antibinding. Of the two possible definitions of a binding region in the molecular plane, the less extended one provides the most sensitive test of the density distribution. The fact that any single charge element in this binding region attracts all three nuclei is a reflection of the gradient of the potential field in this region. The potential surface generated by the three nuclei possesses a trough in this binding region, which next to the potential wells at each nucleus, constitutes the most negative area of the surface. Thus the accumulation of charge in the less extended binding region will lead not only to electrostatic equilibrium, but also to a lowering of the potential energy of the system.

A knowledge of the binding region clearly answers the question as to where charge must be concentrated to lead to a state of electrostatic equilibrium on molecule formation. The next question is concerned with how much charge must be placed in this region. For the problem of comparing various charge distributions, as is intended in this work, the most advantageous way of answering the above question is to pick a standard charge distribution $\rho_0(r)$ which is known to be insufficient from the point of view of the amount of charge it places in the binding region. The difference between the proposed density distribution $\rho(\vec{r})$ and this standard one is then determined. A distribution

$$\Delta\rho(\vec{r}) = \rho(\vec{r}) - \rho_0(\vec{r})$$

with a positive $\Delta\rho$ in the binding regions is a possible distribution. A distribution with a negative $\Delta\rho$ in the binding region is unacceptable as it places less charge density in the binding region than does the standard distribution which is known to be insufficient in this regard. The obvious choice for the standard distribution is that one obtained by placing the nuclei at their equilibrium positions within the molecule, each with its original atomic charge distribution. As will be demonstrated later, such a distribution of charge cannot in general balance the forces of nuclear repulsion on any of the nuclei. This choice of a standard distribution has the added advantage that a plot of $\Delta\rho$ then shows clearly the movement of charge that has occurred

on the formation of the molecule. This method, of plotting the density difference between the isolated atom and the final molecular density, has recently received much attention as a method of understanding what occurs on the formation of a molecule.[6-8]

In the construction of the standard density distribution we choose the z-axis as the axis of quantization and the x-y plane as the molecular plane. Taking the $M = 0$ member of the ^3P ground state of the oxygen atom gives a density of circular contours in the molecular plane and a doubly filled "p_π" orbital.[9] (It is equivalent to the density obtained from the electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^2$.) Added to this is the density obtained from two hydrogen 1s orbitals centered at their proper positions in the water molecule. There are net forces of repulsion acting on all three nuclei with this density distribution. The oxygen density, since it is centrosymmetric, exerts no force on the oxygen nucleus. The oxygen nucleus has, however, penetrated the spherical charge density of each hydrogen atom. Since, according to Gauss's law the field resulting from a spherical charge distribution acts as though all the charge were concentrated at its origin, and only that charge within the sphere defined by the bond length is effective, each hydrogen nucleus is shielded by less than one unit of negative charge from the oxygen nucleus. Thus there is a net force of repulsion on the oxygen nucleus. Each hydrogen nucleus is repelled by the other for the same reason. In addition, there is a net force of repulsion on each hydrogen nucleus due to the oxygen nucleus. If the charge density of the oxygen atom was spherical (equal population of p_x, p_y, and p_z), there would be a net force of repulsion on the hydrogen nuclei. In fact, the density has more p_z (p_π) character than p_x or p_y character, and hence the shielding of the hydrogen nuclei is thus even less than in the spherical case.[10] We have employed the analytical approximations to the SCF wave function for the ^3P state of oxygen as recently derived by Clementi, et al.[11]

There is a complete range of hybridization possible for the oxygen atom in the water molecule: from two lone pairs of pure p character and two bonding orbitals of sp character, through four orbitals all of approximately sp^3 character to two lone-pair orbitals of sp character, and two bonding orbitals of approximately p character. This latter state of hybridization is the one possessed by the oxygen atom in the standard density distribution. The most flexible set of molecular orbitals which can be constructed from the 1s, 2s, and 2p atomic orbitals are (neglecting any slight inner shell polarization)

$$\phi_{b_1} = \lambda(\cos\epsilon_b 2s + \sin\epsilon_b p_1) + \mu(h_1 - \delta h_2) + Vs_0$$

(6) M. Roux, M. Cornille, and L. Burnelle, *J. Chem. Phys.*, **37**, 933 (1962).

(7) M. Roux, S. Besnainou, and R. Daudel, *J. chim. phys.*, **54**, 218 (1956).

(8) C. W. Kern and M. Karplus, *J. Chem. Phys.*, **40**, 1374 (1964).

(9) W. A. Bingel, *ibid.*, **32**, 1522 (1960).

(10) There will be forces of repulsion acting on every nucleus in a collection of neutral atoms in their electronic ground states if (a) the density distribution on each atom is spherical or has more p_π than p_σ character with respect to every other atom in the collection; and (b) the atoms are placed so that half-filled orbitals, if present, overlap (the valence-bond picture of molecule formation). This is a general result with the possible exceptions of the configurations $ns^2 np^1$ and $ns^2 np^2$.

(11) E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1962).

$$\phi_{b2} = \lambda(\cos \epsilon_b 2s + \sin \epsilon_b p_2) + \mu(h_2 - \delta h_1) + Vs_0$$

$$\phi_1 = \cos \epsilon_1 2s + \sin \epsilon_1 p_3$$

$$\phi_2 = \cos \epsilon_1 2s + \sin \epsilon_1 p_4$$

The ϕ_b's are bonding orbitals, λ/μ being a polarity factor and ϵ_b a hybridization parameter which allows for any degree of s–p hybridization. The h_i are hydrogen 1s orbitals which in the molecular density are given an effective nuclear charge of 1.32. The symbols p_1 and p_2 denote 2p orbitals compounded from the $2p_x$ and $2p_y$ orbitals. They do not necessarily point at the two hydrogen atoms, and the angle between p_1 and p_2, termed the orbital angle α, may be greater or less than the bond angle $\mathcal{E}$. The parameter δ is to take account to the fact that the most general molecular orbital description of the water molecule does not necessarily result in bonds localized between only two atoms at a time. It is conveniently termed a delocalization parameter. V is to ensure orthogonality with the inner shell orbital s_0 on the oxygen atom. The angle ϵ_1 is a hybridization parameter for the lone pairs, and p_3 and p_4 are the 2p orbitals in the lone pairs which make an angle of β with one another. The electron density distribution for the molecule is simply (aside from the inner 1s electrons)

$$\rho(\vec{r}) = 2\{\phi_{b1}^2 + \phi_{b2}^2 + \phi_{11}^2 + \phi_{12}^2\}$$

This expression for $\rho(\vec{r})$ is true only when the orbitals are all mutually orthogonal, and thus ϵ_b, ϵ_1, λ/μ, δ, α, and β are not all independent. Three of the parameters may be assigned arbitrary values, and the values of the remaining three are then fixed by the orthogonality conditions. The separate values of λ and μ are obtained by the condition of normalization.

A frequently quoted description of the orbitals in the water molecule[12] is the approximately tetrahedral one in which the angle between the bonding orbitals is equal to the bond angle, i.e., the bonds are not considered to be bent ($\alpha = \mathcal{E}$). This results in lone-pair orbitals with close to sp^3 hybridization. For example, with $\alpha = \mathcal{E}$, $\delta = 0$ (no delocalization), and λ/μ of the order of unity, one obtains lone-pair orbitals with 31% 2s and 69% 2p character. However, the orbitals from oxygen forming the bonds are far from sp^3. With this set of parameters they are in fact 5% 2s and 95% 2p. All four of the orbitals from oxygen can be made approximately sp^3 without bending the bonds by giving to δ a nonzero value. When $\alpha = \mathcal{E}$, $\delta = 0.20$, and $\lambda/\mu = 1.00$, a set of orbitals is obtained in which the lone pairs are 21% 2s and 79% 2p and the bonding orbitals are 27% 2s and 73% 2p. This is termed density I and the plots of $\Delta\rho$ for this density in the molecular plane and perpendicular to it are given in Fig. 2 and 3. The most striking feature of this density distribution is the large amount of charge transferred from the binding region to the antibinding region above the oxygen nucleus. This transfer of density is due almost entirely to the introduction of a $2p_x$ component into the lone-pair orbitals to achieve the sp^3 hybridization. (The standard density for oxygen possesses two sp hybrids perpendicular to the molecular plane with no $2p_x$ contribution.) The accumulation of charge above the oxygen and its depletion below results

(12) J. A. Pople, *Proc. Roy. Soc.* (London), **A202**, 323 (1950); A. B. F. Duncan and J. A. Pople, *Trans. Faraday Soc.*, **49**, 217 (1953).

in a net force on the oxygen nucleus in a direction away from the hydrogen nuclei. This is particularly evident in Fig. 3. The small peak of density immediately below the oxygen nucleus is clearly insufficient to balance the large amount placed above it. There is also a very large amount of charge removed from the immediate vicinity of the oxygen nucleus. This is energetically very unfavorable, as the oxygen nucleus represents the most negative point on the potential surface. Ruedenberg[13] has recently pointed out the necessity of charge buildup at the positions of the nuclei on the formation of molecules from atoms. There are valleys of negative $\Delta\rho$ values between all the nuclei. In a very real sense, a bond must be formed between the two hydrogens in the water molecule, i.e., sufficient charge density must be placed between the nuclei to overcome the nuclear forces of repulsion. Instead of this, the depletion of charge density between the two hydrogens, as found in this density distribution, results in a net force of repulsion. This net force is accentuated by the large accumulation of charge above the oxygen nucleus. Surprisingly enough, the tetrahedral set of orbitals for water leads to a depletion in the charge density in all three overlap regions over what is obtained by simply allowing the original atomic charge distributions to overlap. (Recall that such an overlap of atomic distributions is insufficient to achieve electrostatic equilibrium.) The sp^3-bonding orbitals do lead to the best overlap with the hydrogen orbitals and to the largest transfer of charge to the regions between the oxygen and hydrogen nuclei. However, this is accomplished only at the expense of a large $2p_x$ component being introduced into the lone-pair orbitals. The resulting hybridization transfers density from the binding to the antibinding region and removes more density than was concentrated by the sp^3-bonding orbitals. The lone-pair density is as important in binding the hydrogens as is the density in the bonding orbitals. To label the lone-pair electrons nonbonding is a misnomer. The only important result is the *total* density distribution, not the individual orbital contributions.

The unbalanced charge distribution along the symmetry axis gives rise to a large atomic dipole on the oxygen, much larger than the observed dipole moment. This large atomic moment is partially balanced by the accumulation of charge on the hydrogen nuclei. The buildup of charge on the hydrogens arises from the relatively low λ/μ value and is large enough to give bond polarities $O^{\delta+}-H^{\delta-}$. The ratio λ/μ cannot be increased to place more charge at the oxygen nucleus since the resulting electronic moment would then be many times too large.

As long as $\alpha = \mathcal{E}$ (or if $\alpha > \mathcal{E}$), the plots of $\Delta\rho$ have the same features illustrated for density distribution I regardless of the values assigned to the other parameters. In fact, density I represents the best result obtained for orbitals with $\alpha \geq \mathcal{E}$ after a large number of variations in all the parameters. The reason for the large unfavorable shift in density is due to the $2p_x$ contribution to the lone-pair orbitals. Orthogonality conditions demand that if the bonds are directed at the hydrogens (or if $\alpha > \mathcal{E}$), the lone-pair orbitals must possess a large amount of 2p character. This limita-

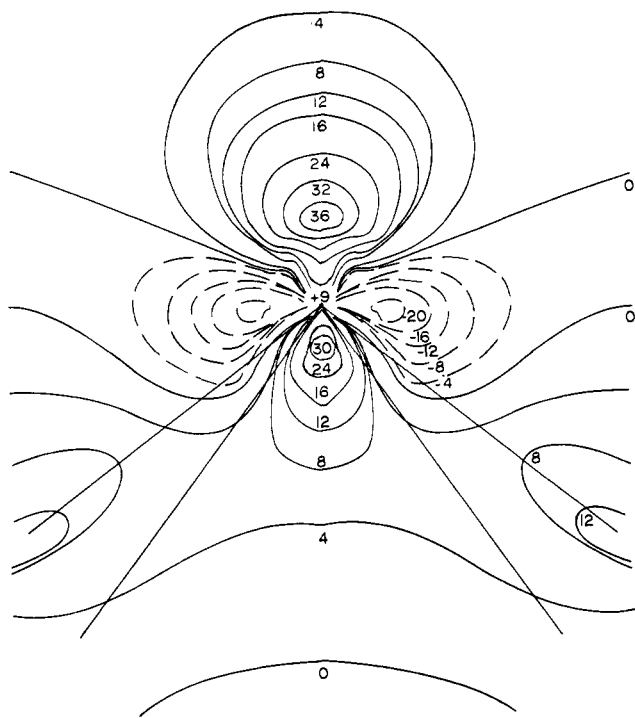(13) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

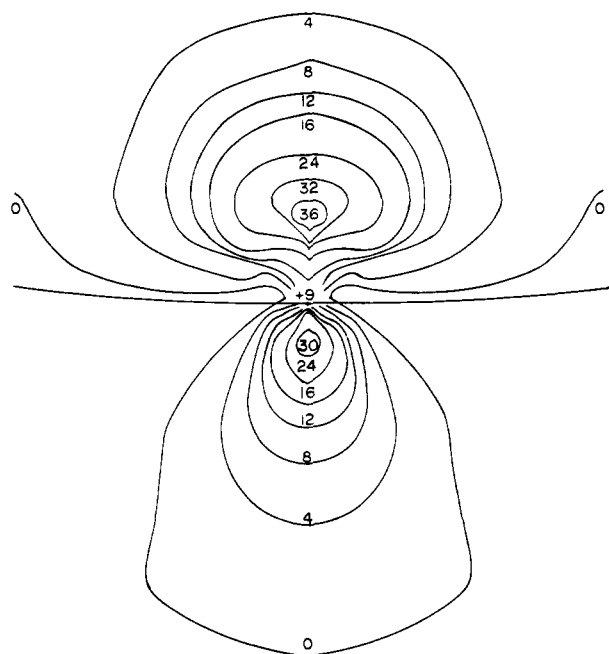Fig. 4.—Plot of $\Delta\rho$ for density distribution II in the molecular plane.

Fig. 5.—Plot of $\Delta\rho$ for density distribution II in the perpendicular plane.

tion can be overcome only by "bending" the bonds. When α is less than ε, the amount of 2p in the bonding orbitals is increased and the amount of 2p character in the lone pairs is decreased. In Fig. 4 and 5 are shown plots of $\Delta\rho$ for a density distribution with bent bonds. It is termed distribution II and has $\alpha = 64°$, $\lambda/\mu = 1.56$, and $\delta = 0.41$. This set of parameters gives bonding orbitals which are 3% 2s and 97% 2p and lone-pair orbitals which are 50% 2s and 50% 2p. The lone-pair orbitals thus contain no 2p contribution in the molecular plane but are simply two sp hybrids directed perpendicularly to this plane, employing the $2p_z$ orbital only. This distribution does concentrate charge
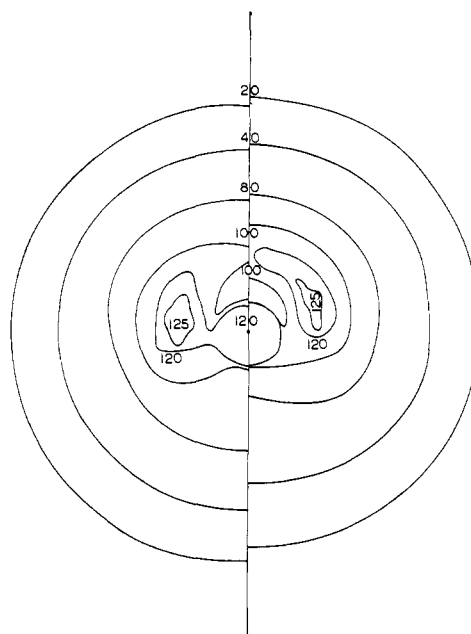

Fig. 6.—Plot of the valence electron density distributions in the perpendicular plane for case I on the right and case II on the left.

density in the binding region, as well as above the oxygen nucleus. The charge is removed from two areas which lie almost entirely within the antibinding regions. The lone pairs in this density distribution do not contribute significantly to $\Delta\rho$ as they are almost unchanged from what they were in the isolated oxygen atom. Instead almost the whole of $\Delta\rho$ is due to a redistribution of the charge originally in $2p_x$ and $2p_y$ orbitals. The density is removed from along the y-axis and concentrated along the x-axis, extending out to the hydrogen nuclei. Charge density is concentrated at each nucleus and between every pair of nuclei. Density distribution II, while not the best obtainable in this range of hybridization, is typical of all cases in which the bonds are bent by at least 15° off the inter-nuclear axis (they are bent by 20° in II) and almost pure 2p in character, the lone pairs are approximately sp hybrids, and δ is not equal to zero.[14] A distribution of this form can lead to electrostatic equilibrium as it concentrates charge in the binding region. Charge is still concentrated above the oxygen nucleus although not to as large an extent as in case I. This results from the increase in the density in the $2p_x$ orbital on oxygen. The same increase in charge density behind the heavy nucleus as well as in the overlap region has been noted by Kern and Karplus[8] in their analysis of Nesbet's SCF wave function for hydrogen fluoride.[15] Such a result is inescapable when the bonding orbital is primarily a p orbital which concentrates density on each side of a nucleus. A distribution such as II can yield the observed dipole moment, not by a large atomic moment (which is almost zero in this case), but through bond moments which for this distribution have the expected polarity $O^{\delta-}-H^{\delta+}$.

Figure 6 is a plot of the *total* electron density functions for distributions I (on the right) and II (on the left) in the plane perpendicular to the molecular plane.

(14) If δ is set equal to zero, there is a large initial overlap of the bonding orbitals with the prominent 2s component of the lone-pair orbitals. The conditions of orthogonality then result in a large transfer of charge from the binding region.

(15) R. K. Nesbet, *J. Chem. Phys.*, **36**, 1518 (1962).

In I more density is clearly accumulated at the top of the molecule as evidenced by the contour lines lying above the corresponding lines in II. Distribution II concentrates more density below the oxygen in the vicinity of the hydrogens (and the binding region). It should be noted that the angle between the maximum density lobes in this plane for distribution II will be less than 180° even though the lone-pair orbitals are sp hybrids. The angle will lie between 150 and 160° as compared to distribution I where it is approximately 120°.

The concept of a binding region together with a knowledge of $\Delta\rho$ for various density distributions allows one to conclude that an acceptable density distribution for the water molecule must possess the following properties: the lone-pair orbitals must be close to sp hybrids, the oxygen orbitals which overlap with the hydrogens must be close to pure 2p orbitals, and the angle between these p orbitals must be considerably less than the bond angle, i.e., the bonds must be bent. Only a density distribution with these characteristics can concentrate charge in the binding regions.[16]

These same requirements for the density function will hold for the ammonia molecule in which the binding region will be approximately pyramidal in shape and enclosed within the pyramidal geometry of the molecule. In this case, the lone pair must necessarily be close to a pure 2s orbital and the bonds, again bent, close to pure 2p orbitals from the nitrogen. These features of the density distributions for the water and ammonia molecules have been pointed out before,[17,18] but this was accomplished by attempting a detailed force calculation for these molecules using Slater orbitals. This work has been criticized by Alexander and Salem[19] on the grounds that simple Slater functions

do not give an adequate enough description of the density for regions close to the nuclei. The present approach to the problem is meant to meet this objection in two ways. The use of SCF orbitals for the oxygen removes the objection regarding the inadequacy of the Slater orbitals. More important, a knowledge of the sign and magnitude of $\Delta\rho$ throughout the binding region excludes certain ranges of values for the parameters governing the degree of hybridization, etc., and does this regardless of the precise forms chosen for the orbitals. Thus it was found that the general forms of the plots of $\Delta\rho$ for the distributions exhibit only minor variations in magnitude if Slater rather than the SCF orbitals are employed, or if the orbital exponents are varied.

Full advantage has not been taken of the rigorous electrostatic approach to chemical binding. The knowledge that a chemical bond is the result of the accumulation of negative charge density in the binding region to the extent necessary to balance the nuclear forces of repulsion is a simple concept often overlooked. The electrostatic approach focuses attention on the three-dimensional electron density distribution in a molecule. Very few plots of ρ or $\Delta\rho$ have been given in the literature, and the effects of hybridization on the density are not at all as they are frequently pictured. The statement of Mulliken[20] that a little hybridization goes a long way is clearly brought to light by a $\Delta\rho$ plot. For example, in the present case, extreme rehybridization of the oxygen lone-pair density on the formation of the water molecule results in a large unfavorable shift in the density distribution. The electrostatic concept clearly demonstrates the important bonding role the lone-pair density plays in this molecule. Such results are difficult to appreciate on purely energetic grounds.

(16) The SCF LCAO–MO calculations for the water molecules by H. Shull and F. O. Ellison, *J. Chem Phys.*, **23**, 2348 (1955), when transformed into equivalent orbitals have these very properties: lone pairs, 53% 2p character; bonding orbitals, almost 100% 2p from oxygen; and an orbital angle of 69°.

(17) R. F. W. Bader and G. A. Jones, *Can. J. Chem.*, **41**, 586 (1963).

(18) R. F. W. Bader and G. A. Jones, *J. Chem. Phys.*, **38**, 2791 (1963).

(19) L. Salem and M. Alexander, *ibid.*, **39**, 2994 (1963).

(20) R. S. Mulliken, *ibid.*, **19**, 900 (1951).

[Contribution from the Department of Synthetic Chemistry, Nagoya University, Chikusa-ku, Nagoya, Japan]

Electrophoresis of a Polyelectrolyte in Solutions of High Ionic Strength

By Ichiro Noda, Mitsuru Nagasawa, and Mitsuru Ōta

Electrophoretic mobilities of poly(sodium acrylate) of different degrees of neutralization were determined in 0.1 N NaCl solution. It was found that the mobility is independent of molecular weight and equal to the mobility of segment. This result is in good agreement with the theories of Hermans–Fujita, Overbeek–Stigter, and Hermans. It may be concluded that the polyion coil is free draining in electrophoresis at high ionic strength, in remarkable contrast to the behavior of the polyion in viscous motion.

Introduction

Various transport phenomena such as viscosity, sedimentation, diffusion, and electrophoresis are fundamental for clarifying the hydrodynamic behavior of a polyion coil in solution. Among these, the electrophoresis is unique in the feature that the polyion and the counterions move in opposite directions, while the polyion moves together with the counterions in viscosity, sedimentation, and diffusion.

Theories of the electrophoresis of the linear polyelectrolytes have been presented by Hermans and Fujita,[1] Overbeek and Stigter,[2] and Hermans.[3] These theories differ in mathematical development but yield essentially the same results; this arises from the fact that they all use the same model, i.e., the partially

(1) J. J. Hermans and H. Fujita, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **B58**, 182 (1955).

(2) J. Th. G. Overbeek and D. Stigter, *Rec. trav. chim.*, **75**, 543 (1956).

(3) J. J. Hermans, *J. Polymer Sci.*, **18**, 529 (1955).