

- (6) J. P. Schroeder and D. C. Schroeder, *J. Org. Chem.*, **33**, 591 (1968).
 (7) J. W. Park and M. M. Labes, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 147 (1977).
 (8) A. C. Griffin, unpublished work.
 (9) L. Verbit, *Mol. Cryst. Liq. Cryst.*, **15**, 89 (1971).
 (10) M. Sorai, T. Nakamura and S. Seki, *Pramana, Suppl. 1*, 503 (1975).
 (11) (a) J. B. Flannery and W. Haas, *J. Phys. Chem.*, **74**, 3611 (1970); (b) P. R. Patel, *J. Indian Chem. Soc.*, **50**, 514 (1973).
 (12) (a) J. Billard, *C. R. Hebd. Seances Acad. Sci., Ser. B*, **280**, 573 (1975); (b) G. W. Smith and Z. G. Garlund, *J. Chem. Phys.*, **59**, 3214 (1973); (c) J. B. Flannery and W. Haas, *J. Phys. Chem.*, **74**, 3611 (1970).
 (13) See paragraph at end of paper regarding supplementary material.
 (14) J. S. Dave and R. A. Vora, *Pramana, Suppl. 1*, **447** (1975).
 (15) A. P. Kovshik, Y. I. Denite, E. I. Ryumtsev, and V. N. Tsvetkov., *Kristallografiya*, **20**, 861 (1975).
 (16) L. Kofler and A. Kofler, "Thermomikromethoden", Verlag Chemie, Weinheim/Bergstr., Germany, 1954.
 (17) J. Billard, *Bull. Soc. Fr. Mineral. Cristallogr.*, **95**, 206 (1972).
 (18) J. P. Van Meter and B. H. Klanderma, *Mol. Cryst. Liq. Cryst.*, **22**, 271 (1973).
 (19) A. C. Griffin, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 141 (1977).
 (20) (a) Reference 1, p 197 ff; (b) see G. W. Gray and P. A. Winsor, Ed., "Liquid Crystals and Plastic Crystals", Vol. 1, Ellis Horwood, Chichester, England, 1974, pp 116-121.
 (21) We wish to thank Dr. P. E. Cladis for a preprint of this work.
 (22) As pointed out by a referee we are unable a priori to rule out complexation through terminal groups themselves. Of interest in this regard is the fact that a mixture of cholesteryl palmitate and 1I gives rise to a slightly enhanced $S_A \rightarrow I$ temperature. There is of course no aromatic ring in cholesteryl palmitate, but it does possess a carbonyl group which could participate in a charge transfer interaction.
 (23) J. F. Johnson, G. J. Bertolini, and A. C. Griffin, Abstracts, Seventh North American Thermal Analysis Society Conference, St. Louis, Mo., Sept 1977, No. 24.

Valence Shell Electron Pair Repulsions and the Pauli Exclusion Principle

Michael B. Hall

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received May 2, 1977

Abstract: The basic tenet of the valence shell electron pair repulsion (VSEPR) model, that the Pauli exclusion principle determines the molecular geometry, has been examined by direct ab initio calculations on H₂O. The calculations include one-electron models, which have Pauli forces but no electron-electron repulsions, and Hartree models, which have electron-electron repulsion but no Pauli forces. The latter calculations strongly suggest that as the Pauli restriction is removed the H₂O angle decreases. This behavior, which is opposite that expected by VSEPR, indicates that the dominant Pauli repulsions in H₂O are between the bond pairs. The calculations show that the optimum hybridization is relatively independent of the H-O-H angle. Thus, the hybrids appear to have some intrinsic existence and are not formed solely to provide better O-H bonding and are not always directed toward the hydrogens. The intrinsic hybridization is shown to be controlled by the number of electrons in the valence shell. This result provides a connection between traditional localized valence concepts and Walsh's rule. The driving force for the formation of these hybrids is, of course, the system's desire to keep the lower energy 2s orbital as fully occupied as possible, i.e., as a lone pair. Thus, the stereochemical activity of the lone pairs is, in reality, the stereochemical activity of the 2s orbital. A simple model based on these concepts is useful in predicting the geometry of a variety of AH_n systems, particularly why the angles decrease so dramatically when a first-row central atom is replaced with one from the second row, i.e., from H₂O to H₂S.

Introduction

Of the two most popular models for rationalizing and predicting molecular structure, Walsh's rules¹ and valence shell electron pair repulsion (VSEPR),² only Walsh's rules have been subject to extensive theoretical investigation and justification.³ Although VSEPR appears to work quite well, its physical basis is still unclear. Its basic assumption is that the Pauli exclusion principle forces electron pairs to occupy different regions of space. It is important to note that the repulsions between pairs of electrons are attributed to the Pauli principle (Pauli repulsions) and not to electrostatic repulsions. This assumption is based on the early work of Lennard-Jones, who showed that in the absence of all other forces, the Pauli principle will force particles of like spin to occupy different regions of space.⁴ Recently, Thompson has presented a similar model as justification for VSEPR.⁵

For a real molecule the question is, will the Pauli principle still be the dominant factor in determining the geometry when there are other strong forces present. Several authors have justified VSEPR by comparing its predictions of the geometry with those of other models. Thus, Allen has shown that the VSEPR and Walsh's rules parallel each other.⁶ The similarity between the predictions of extended Hückel theory and VSEPR has been pointed out by Bartell and Plato.⁷ Schnuelle and Parr have made a connection between their valence bond

model and VSEPR,⁸ while Nakatsuji has shown the equivalence of the results of his force model with VSEPR.⁹ Comparisons have been made between VSEPR and accurate self-consistent field calculations with conflicting results. Trindle and Weiss, using the floating spherical Gaussian model, found that the total electron repulsion parallels the total energy.¹⁰ They interpreted this as supporting the VSEPR model. However, Naleway and Schwartz, using a very large basis for calculations on H₂O, were not able to find an intuitively satisfying way of partitioning the total energy which would totally support VSEPR.¹¹

However, none of these investigations has examined the actual physical basis of the VSEPR model itself. In the first direct study of the effect of the Pauli principle on the geometry, Bader and Preston have shown that its effect is in the opposite direction from that assumed by VSEPR, i.e., the Pauli principle has the effect of increasing the angles in H₂O and NH₃ from tetrahedral values rather than decreasing the angle as suggested by VSEPR.¹² In a recent paper, Bills and Snow have suggested that the previous work of Bader and Preston is open to ambiguous interpretation.¹³ However, they agree with Bader and Preston that the Pauli principle is not responsible for the geometry of molecules. One of their key arguments is the fact that a one-electron model calculation for H₂O predicts a linear molecule. Their conclusion that one-electron models do not predict the correct geometry is at variance with the results of

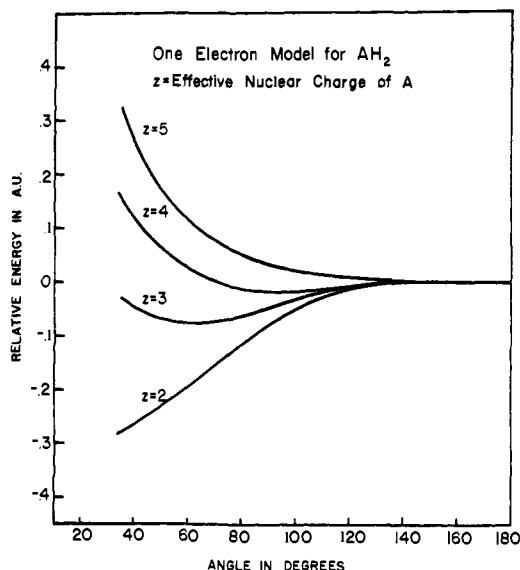


Figure 1. Total energy of the one-electron model of AH_2 vs. H-A-H angle for several effective nuclear charges.

Schmidtke and Preuss using similar methods¹⁴ and with the long experience of extended Hückel theory. Furthermore, none of the studies which criticize the theoretical basis of VSEPR offers an explanation of why it works.

In this work we will show that realistic one-electron models will predict the correct geometry. We will then examine the question of how the Pauli principle affects the geometry by systematically violating the Pauli principle and examining the effect on the geometry. We will also address ourselves to the question of why VSEPR works if it is not totally determined by the Pauli exclusion principle.

Results and Discussion

Noninteracting Electrons. Lennard-Jones has shown that in the absence of other forces, the Pauli principle will force electrons of like spin confined to the surface of a sphere to remain as far apart as possible.⁴ Thus, if there are four electrons on the sphere, they will adopt a tetrahedral arrangement. The question before us is how will the other forces in a molecule modify this picture, and to what degree is the Pauli effect still dominating the geometry? Bills and Snow examined this question by studying the geometry of a water molecule with noninteracting electrons.¹³ They examined the geometry predicted by a calculation on H_2O^{9+} in which the total energy was calculated from the orbital energy of the lowest five orbitals. This calculation adds rather strong electron-nuclear attraction and nuclear-nuclear repulsion to the effect of the Pauli principle. They found that a linear H_2O molecule was predicted from this calculation. Thus, the additional forces were strong enough to override any effect of the Pauli principle.

We have reexamined this question in detail by studying the geometry predicted for the AH_2 system, where we have varied the effective nuclear charge on A. The free electron Hamiltonian

$$H = \sum_{i=1}^n \left(-\frac{1}{2} \nabla_i^2 - \frac{Z_A}{r_{Ai}} - \frac{1}{r_{H1i}} - \frac{1}{r_{H2i}} \right) \quad (1)$$

includes the kinetic energy and the electron-nuclear attraction, but no electron-electron repulsions. The molecular orbitals (MOs) are expanded as a linear combination of atomic orbitals. The 1s, 2s, and 2p atomic orbitals for A are the appropriate Slater-type orbitals corresponding to the effective nuclear charge Z_A , while the 1s atomic orbital for H is for unit

charge.¹⁵ Although these functions provide accurate solutions to the free-electron atomic Hamiltonians, the MO expansion using these orbitals may not be as accurate. Thus, we have augmented this basis with 3s, 3p, and 3d functions on A and 2s and 2p functions on H. The A-H bond distance was fixed arbitrarily at 2.00 au. The results for this calculation are shown in Figure 1, where we have plotted the total energy, including the nuclear-nuclear repulsion not shown in eq 1, as a function of H-A-H angle for several different effective nuclear charges. For effective nuclear charges greater than 5, a totally repulsive curve is obtained and one would predict a linear AH_2 system. These results are similar to those of Bills and Snow.¹³ However, for effective nuclear charges of 4 or less, we find a minimum in the total energy. This result parallels those of Schmidtke and Preuss.¹⁴ The curve for $Z = 4.0$ has a minimum very near the equilibrium angle of water; however, the minimum is much too shallow. As the effective nuclear charge is reduced, this minimum becomes deeper and shifts to smaller angles. One should not expect this simple model to yield accurate potential curves, but it does parallel the VSEPR model in the sense that as the relative electronegativity of the ligands (H's) increases, the angle decreases, i.e., F_2O has a smaller angle than H_2O . Even the totally repulsive curve, such as that for $Z = 5$, has an experimental analogue in Li_2O . Li_2O has long been taken as an example of the failure of VSEPR. The reasons for this failure are apparent if we examine the electron distribution for AH_2 when $Z = 5$. The effective nuclear charge on A is sufficiently large that the filled MOs are over 80% localized on A and, therefore, the H's appear as nearly bare protons. In this situation the electron distribution around A is nearly independent of the positions of these protons and the geometry and energy are dominated by the H-H nuclear repulsions. The analogy to Li_2O is borne out by calculations of Allen⁶ which showed that the molecule is best described as $Li_2^+O^{2-}$.

Although these results will be mitigated by the electron-electron repulsions, the fact that this one-electron model does parallel the VSEPR model suggests that the linear results for high effective nuclear charge do not disprove the involvement of the Pauli principle. In this regard, a model calculation which obeys the Pauli principle but which does not predict the correct geometry, because it is unrealistic in other ways, does not constitute proof that the Pauli principle is not involved. However, the calculations do show that in the presence of other forces, the Pauli principle will not always control the geometry.

Interacting Electrons. In order to provide a realistic assessment of the importance of the Pauli principle in determining the geometry of molecules, we will examine a real molecular system under systematic violations of the Pauli principle. One must be careful to define what one means by a violation of the Pauli principle. VSEPR uses the Pauli principle in describing repulsions of valence electrons which are grouped into bond pairs and lone pairs. Thus, they are concerned with what the effect of the Pauli principle is on bond formation. We will examine the effect of the Pauli principle in this context by removing the Pauli restriction in two stages. First, we can remove antisymmetry requirement and write the total wave function as a simple product of molecular orbitals. This is essentially the Hartree product wave function. If we restrict the orbitals to remain orthogonal, a real restriction for a Hartree product function, we will still satisfy a major part of the Pauli principle because the orthogonality will constrain electron pairs to different regions of space. In the second stage we will remove the orthogonality restriction. Now the electrons will be free to occupy the same regions of space and the Pauli principle will be more severely violated.

The Hartree product wave function is

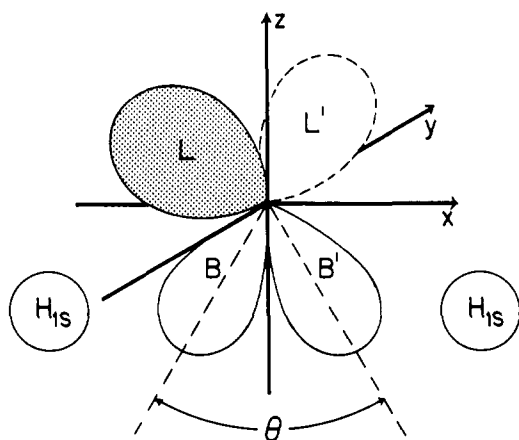
$$\psi = \phi_1 \bar{\phi}_1 \phi_B \bar{\phi}_B \phi_B \bar{\phi}_B \bar{\phi}_L \bar{\phi}_L \phi_L \bar{\phi}_L \quad (2)$$

where *l*, *B*, and *L* refer to inner shell, bond pair, and lone pair, respectively. The total energy of this wave function is

$$E = \sum_i^n 2(T_{ii} + V_{ii}) + \sum_i^n \sum_j^n (2 - \delta_{ij})J_{ij} + \sum_{A>B} \sum \frac{Z_A Z_B}{R_{AB}} \quad (3)$$

where the sum runs over the doubly occupied orbitals, *T* is the kinetic energy, *V* is the electron-nuclear attraction, *J* is the electron-electron (Coulomb) repulsion, and the last term is the nuclear-nuclear repulsion. Note that there are no exchange integrals in this energy expression as they arise from the antisymmetry properties of a wave function. As Levy, Nee, and Parr have pointed out, the Hartree function provides a classical picture of the bonding, in that Hartree orbitals will be highly localized.¹⁶ Even though the energy and wave function appear simpler than the full Hartree-Fock case, their solution is complicated by the fact that this problem cannot be formulated as a simple eigenvalue problem, because the wave function is not invariant to a unitary transformation.

Since the Hartree orbitals should be localized, we have chosen a simple localized model with only two variational parameters. In the coordinate system, θ represents the angle



between the bond pair hybrids, not necessarily the same as the H-O-H angle, i.e., the hybrids are not constrained to point toward the H positions. If we define two coefficients as

$$c = 1.0/\tan(\theta/2) \text{ and } c' = (1 - c^2)^{1/2} \quad (4)$$

the bond pair hybrids can be written as

$$\phi_{BH} = (c'\chi_{2s} - c\chi_{2p_z} \pm \chi_{2p_x})/\sqrt{2} \quad (5)$$

and the lone pair hybrids as

$$\phi_L (c\chi_{2s} + c'\chi_{2p_z} \pm \chi_{2p_y})/\sqrt{2} \quad (6)$$

for equivalent lone pairs, or as

$$\begin{aligned} \phi_L &= \chi_{2p_y} \text{ and} \\ \phi_{L'} &= c\chi_{2s} + c'\chi_{2p_z} \end{aligned} \quad (7)$$

for nonequivalent lone pairs. The bonding molecular orbital can be written as

$$\phi_B = N((1 - \lambda^2)^{1/2}\phi_{BH} + \lambda\chi_{1sH}) \quad (8)$$

Both θ and λ are varied to minimize the energy. The atomic basis functions were chosen as the best atom exponents¹⁵ of Clementi and Raimondi.¹⁷ Although these are not the optimum exponents, especially 1.0 for H, the qualitative results will not be altered by using other exponents. The O-H distance was fixed at its equilibrium value, 1.81 au. An initial value of θ and λ was chosen. The inner shell, lone pair (eq 6 or 7) and bond pair (eq 8) orbitals were calculated. In the case of the

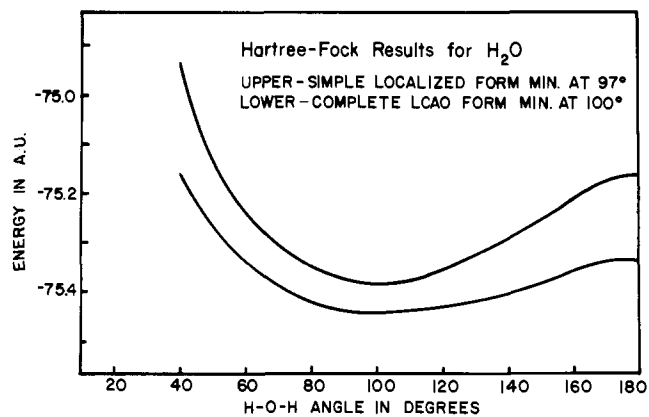


Figure 2. Total energy of H₂O vs. H-O-H angle for the Hartree-Fock wave functions. Upper curve is localized model. Lower curve is complete LCAO model.

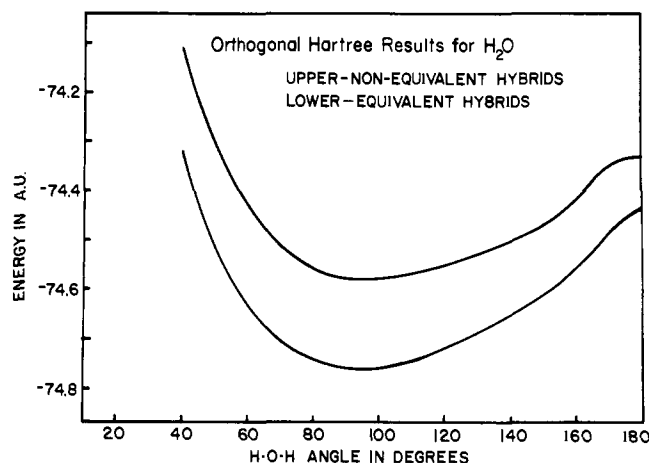


Figure 3. Total energy of H₂O vs. H-O-H angle for the orthogonal Hartree wave functions. Upper curve is for nonequivalent lone pairs. Lower curve is for equivalent lone pairs.

orthogonal Hartree method, these were symmetrically orthogonalized using the Löwdin procedure,¹⁸ which in a least-squares sense produces orthogonal orbitals most like the original ones. The energy was then calculated according to eq 3. This procedure was incorporated into a modified Newton-Raphson iteration¹⁹ and the energy was minimized with respect to the parameters θ and λ .

For comparison we have also calculated the Hartree-Fock-Roothaan results in this basis both with the complete LCAO MO form using POLYATOM²⁰ and with our localized model. Although our localized model does not incorporate all the variational freedom of the complete LCAO calculation, the similarity of the potential curves shown in Figure 2 suggests that it does incorporate the most important parts, i.e., the 2s-2p mixing (θ) and the O-H mixing (λ). Its total energy is slightly greater, the minimum in the energy occurs at an angle 3° smaller, and the minimum is somewhat deeper. The results for the orthogonal Hartree functions are shown in Figure 3. The two curves represent the different choice for the lone pairs (equivalent or nonequivalent). Interestingly, the energy difference between these two simple Hartree product functions parallels the energy difference observed in the accurate generalized valence bond calculations of Hunt, Hay, and Goddard.²¹ They found the equivalent hybrid form to be 2 kcal lower in energy than the nonequivalent form. The Hartree energy of our calculations magnifies these differences because it does not include any exchange. Both curves look quite similar to the

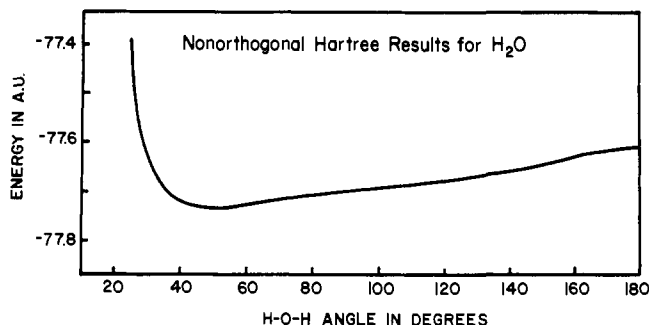


Figure 4. Total energy of H_2O vs. H-O-H angle for the nonorthogonal Hartree wave function.

Hartree-Fock result, which is invariant to this transformation of the lone pairs; however, the depth of the minimum has been increased and the minimum occurs at an angle 1° smaller (average value). The strong similarity between the Hartree and Hartree-Fock results suggests that the exchange integrals are not critical in determining the gross geometry. Apparently the antisymmetry of the wave function is not critical for the geometry as long as the orbitals remain orthogonal. This suggests the possibility of developing a classical picture of the geometry based on orthogonal Hartree wave functions. However, if we remove this orthogonality restriction, a more severe violation of the Pauli principle occurs. Although eq 3 would not be the correct expression for the energy of an antisymmetric wave function formed from nonorthogonal orbitals, it is the correct expression for a simple Hartree product function for both orthogonal and nonorthogonal orbitals as long as the orbitals are normalized. In Figure 4, we find that when the orthogonality restriction is removed, the energy drops precipitously and we do not get a minimum until about 45° , where the nuclear repulsion begins to dominate. There is a large relatively constant drop in the total energy (~ 3 au), which arises because of the loss of orthogonality between the 1s and 2s O orbitals; however, because of the minimal basis there is no collapse of the wave function into the core. Thus, when the Pauli principle is more severely violated, the H-O-H angle decreases. This strongly suggests that Pauli forces are mainly repelling the two hydrogens or bond pairs in H_2O and that lone pair Pauli repulsions are physically important for the geometry. In a minimal basis calculation, which is usually satisfactory for the gross features of the geometry, the major nonorthogonality, which arises when O and H form H_2O , comes from H-H overlap and O-H overlap. The small angle for the nonorthogonal case arises from the loss of H-H and H-O Pauli repulsions. In a sense, the system is forming a H-H bond while retaining the O-H bonds, a situation which cannot occur with orthogonal orbitals.

In the preceding calculations we have left intact the "atomic" effects of the Pauli principle, i.e., we have kept the oxygen valence orbitals orthogonal. Thus, we have not fully relaxed the Pauli principle, but we have tried to examine the effect of the Pauli principle on molecular formation, although the separation of "atomic" and "molecular" effects is by no means rigorous. If we were to totally relax the "atomic part" of the Pauli principle, all the electrons in H_2O would shift to the O 1s orbital until the electron-electron repulsions were large enough to populate the 2s or higher orbitals. The most likely result would be the trivial situation of an O^{2-} ion and two bare protons with a linear geometry. We did not deem it profitable to study this situation in detail. However, we have made several calculations in which the orthogonality between bond pairs and lone pairs was relaxed. The lowest energy solution, again, has an equilibrium angle near 40° . The bond pair

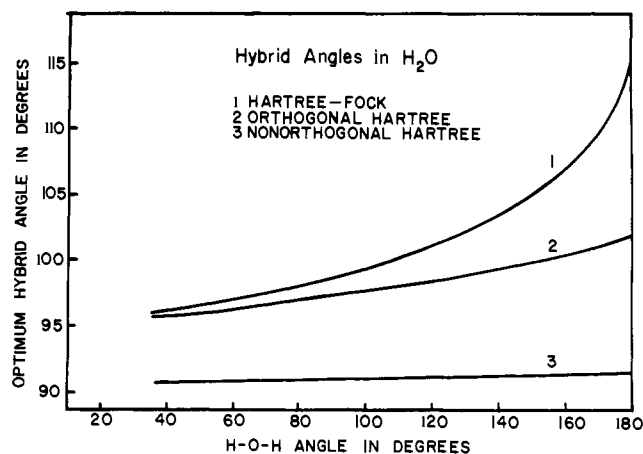


Figure 5. Optimum hybrid angle (θ) vs. H-O-H angle. Curves are for Hartree-Fock wave function (1), orthogonal Hartree wave function (2), and nonorthogonal Hartree wave function (3).

hybrids are nearly pure 2p, while the lone pair hybrids are both pure 2s, even though they both have the freedom to mix in the other atomic component. Again, this is in contrast to what one would expect based on VSEPR. We will present some arguments in the next section, which will clarify why the lone pairs collapse to 2s functions and why there is no 2s character in the bond pairs.

If we reject the VSEPR model, we must offer alternative explanations of the observed geometries. Walsh diagrams offer one alternative; however, it would be more satisfying if we could offer a localized electron model which would also explain why VSEPR has had such success. A clue to this problem can be found by examining how θ , the optimum angle between hybrids, varies with the geometric H-O-H angle. The results are shown in Figure 5. As the geometry is varied over a wide range (40 – 180°), the optimum hybrid angle changes very little, the largest change (97 – 115°) being for the Hartree-Fock wave function. Although these results are somewhat dependent on our model and on the small basis set employed, they are corroborated by several other studies. Naleway and Schwartz found a similar situation in the localized orbitals of H_2O with a basis set large enough to be near the Hartree-Fock limit.¹¹ Likewise, Klessinger found a relatively small variation in the angle between bond hybrids in his self-consistent group function study of water.²² Nakatsuji uses the idea that the hybrids follow behind the nuclear movements in his force analysis of molecular structure.²³ Apparently the optimum hybridization in H_2O has an existence independent of the H-O-H angle and has a strong influence on the actual geometry.

If the geometry is being determined by the hybridization, what determines the hybridization? To examine this question, we have studied the optimum hybrid angle as a function of the number of electrons. Using the orthogonal Hartree functions (nonequivalent) with the H-O-H angle fixed arbitrarily at 110° , we have examined the optimum hybrid angle as a function of the number of lone pair electrons. The results are shown in Figure 6. With two lone pairs the optimum hybrid angle is 101° , which suggests that the bond angle, now 110° , would close up toward this hybrid angle to lower the energy. If we remove an electron pair from the pure 2p orbital, the optimum hybrid angle changes to 116° , which indicates a larger angle for this system. This increase in the hybrid angle is not due to any change in the Pauli repulsions since the orbital from which we removed the pair of electrons is a pure 2p and is orthogonal by symmetry to the other electron pairs. As further evidence that this is not an effect of the Pauli principle, we can recall that in a simple one-electron model, which obeys

the Pauli principle, the energy of this orbital is independent of the geometry. A close examination of the energy contributions suggests that removal of this pair of electrons decreases the electron-electron repulsions such that the electrons which were previously localized in the other lone pair can now lower the electron repulsions further by distributing themselves more equally with the bond pair. Thus, this change in hybridization is strongly connected to the details of the two-electron energy and not to the Pauli principle.

When the next lone pair is removed, we find a much more radical opening of the optimum hybrid angle to 165° , even though the H-O-H angle remains fixed at 110° . We must conclude that the optimum hybrid angle is strongly controlled by the number of electrons and only weakly influenced by the actual positions of the hydrogens. The reason for this radical behavior is the system's desire to keep the 2s orbital of oxygen occupied, because of its lower energy. Thus, after removing the second lone pair of electrons, we have severely depopulated the oxygen 2s orbital. Because this orbital is lower in energy than the oxygen 2p orbital, the system can lower its total energy by increasing the occupation of the 2s, i.e., by changing the hybridization from about sp^2 to nearly sp . Thus, a lone pair of electrons prefers to remain as purely 2s as possible to avoid placing much 2s character in the empty antibonding orbitals. In other words, as the bond hybrids mix in 2s character, the 2s loses electron density, because bond formation will place 2s character into the empty antibonding orbitals. Therefore, the lowest energy situation will be that in which the 2s is primarily lone pair in character. Support for this view comes from the accurate generalized valence bond study on water by Hunt, Hay, and Goddard.²¹ They found that the bond pairs are 82% 2p while the lone pairs are 59% 2p. The latter value corresponds to equivalent lone pairs. If we convert this to a pure 2p perpendicular to the molecular plane, the remaining lone pair in the molecular plane would be 82% 2s. The recent accurate valence bond calculations of Chipman, Kirtman, and Palke show similar differences, though not as dramatic. Their calculations also show that "each oxygen bonding orbital is bent in from the corresponding OH internuclear line by about 5° ".²⁴ We would interpret this as oxygen's attempt to further reduce the angle and increase the 2s occupation, but failing because of the resistance of the Pauli repulsions between the hydrogens.

Conclusions

Our basic view of the geometry is quite similar to traditional concepts of localized valence.²⁵ There are, however, some important differences. Rather than the direction of the hybrids being controlled by the location of the ligands, they are controlled by the total number of valence electrons. This provides a strong link between the localized valence description and the delocalized one provided by Walsh's rules. Thus, this intrinsic hybridization, rather than being merely a mathematical convenience, is in fact controlling the geometry. The driving force for this behavior is the system's desire to lower its total energy by keeping the lower energy 2s orbital as fully occupied as possible. Thus, we emphasize the promotion energy as a dominate factor; this point of view is also taken by Musher in his description of hypervalence,²⁶ and is also supported by studies of the effect of $2s \rightarrow 2p$ promotion on the geometry.²⁷ The Pauli principle acts mainly to open up the bond angles over those suggested by maximum 2s occupation. It has the effect of increasing the 2s character in the bonds, thus mitigating the desire of 2s to remain as a lone pair. In our view, the lone pairs have no difficulty satisfying the Pauli principle because they are not confined to particular regions of space as are bonding orbitals. This freedom, rather than providing strong repulsion between lone pairs, simply allows them to avoid other electrons without causing geometric distortions. In our view, the ste-

HYBRID ANGLE VS. NUMBER OF ELECTRONS

H-O-H Angle Maintained at 110°

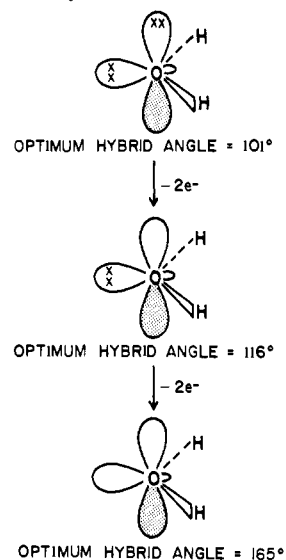


Figure 6. Optimum hybrid angle (θ) as a function of the total number of valence electrons. The geometric H-O-H angle is fixed at 110° .

reochemical activity of lone pairs arises instead from the desire to minimize the total energy by keeping the 2s totally occupied. The important Pauli repulsions are those between the bond pairs, because here the electrons cannot avoid each other as the geometry changes because they are confined to be close to the nuclei. Although the bond hybrids do not necessarily point toward the nuclei, the bonding orbital is a linear combination of two (or more) bond hybrids from different atoms which results in the electron density being directed near the line joining the two nuclei.

A simple model based on these ideas is consistent with the geometry of first-row hybrids. For OH_2 , maximum 2s occupation will occur if the bonding is only through the 2p orbitals (90°). However, the Pauli repulsions between the hydrogens open up this angle to 104° . Again, for NH_3 maximum 2s will occur if it is a pure lone pair and the bonding occurs only through the 2p (90°). Because there are 3 H's, the Pauli repulsions will be larger and the angle will open up to 107° (greater than in H_2O). In CH_4 , the Pauli repulsions and maximum 2s occupation both occur for tetrahedral geometry. For BH_3 , the maximum 2s will occur if the empty orbital is pure 2p; therefore, we find a trigonal planar structure. This structure also minimizes the Pauli repulsions. Likewise for BeH_2 , if the two empty orbitals are pure 2p, maximum 2s occupation will result and the molecule will be linear. We believe that our model offers a simple explanation of the geometry of the second-row hydrides, H_2S and PH_3 . The larger size of the central atom reduces the Pauli repulsions between the hydrogens so that the pressure to keep the 3s totally occupied is able to force the angles down to nearly 90° .

Of course the exact geometry of any real molecular system is a balance between a number of forces, and we do not wish to imply that our description can account for all geometric subtleties. Further work on the Hartree product wave function and the effects of orthogonality with larger basis will be necessary.²⁸ However, we do believe that Pauli repulsions between bond pairs (not lone pairs) and the pressure to keep the ns orbital occupied play a fundamental role in the geometry. Further support for this view comes from a study of the Walsh diagrams on a variety of systems, where we show that the ns - np energy separation controls the curvature of the energy levels.²⁹

Acknowledgment. The authors would like to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation for support of this research.

References and Notes

- (1) A. D. Walsh, *J. Chem. Soc.*, 2260, 2266, 2288, 2296, 2306 (1953).
- (2) R. J. Gillespie and R. S. Nyholm, *Q. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *Angew. Chem., Int. Ed. Engl.*, **6**, 819 (1967).
- (3) R. J. Buenker and S. P. Peyerimhoff, *Chem. Rev.*, **74**, 127 (1974).
- (4) J. E. Lennard-Jones, *J. Chem. Phys.*, **20**, 1024 (1952).
- (5) H. B. Thompson, *J. Am. Chem. Soc.*, **97**, 5293 (1975).
- (6) L. C. Allen, *Theor. Chim. Acta* **24**, 117 (1972).
- (7) L. S. Bartell and V. Plato, *J. Am. Chem. Soc.*, **95**, 3097 (1973).
- (8) G. W. Schnuelle and R. G. Parr, *J. Am. Chem. Soc.*, **94**, 8974 (1972).
- (9) H. Nakatsuji, *J. Am. Chem. Soc.*, **95**, 345, 354, 2084 (1973).
- (10) C. Trindle and L. C. Weiss, *J. Phys. Chem.*, **79**, 2435 (1975).
- (11) C. A. Naleway and M. E. Schwartz, *J. Am. Chem. Soc.*, **95**, 8235 (1973).
- (12) R. F. W. Bader and H. J. T. Preston, *Can. J. Chem.*, **44**, 1131 (1966).
- (13) J. L. Bills and R. L. Snow, *J. Am. Chem. Soc.*, **97**, 6340 (1975).
- (14) H. H. Schmidtke and H. Preuss, *Z. Naturforsch. A*, **16**, 790 (1961); H. H. Schmidtke, *ibid.*, **17**, 121 (1962); **18**, 496 (1963).
- (15) The Slater-type orbitals were expanded in four Gaussian type functions according to R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).
- (16) M. Levy, T. Nee, and R. G. Parr, *J. Chem. Phys.*, **63**, 316 (1975).
- (17) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
- (18) P. O. Lowdin, *J. Chem. Phys.*, **18**, 365 (1950).
- (19) D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).
- (20) POLYATOM (II), QCPE Program No. 199, Indiana University, Bloomington, Ind.
- (21) W. J. Hunt, P. J. Hay, and W. A. Goddard III, *J. Chem. Phys.*, **57**, 738 (1972).
- (22) M. Klessinger, *Chem. Phys. Lett.*, **4**, 144 (1969).
- (23) H. Nakatsuji, *J. Am. Chem. Soc.*, **96**, 24, 30 (1974).
- (24) D. M. Chipman, B. Kirtman, and W. E. Palke, *J. Chem. Phys.*, **65**, 2556 (1976).
- (25) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 120; C. A. Coulson, "Valence", 2nd ed, Oxford University Press, London, 1961, pp 163, 179, 221.
- (26) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).
- (27) J. Jarvie, W. Willson, J. Doolittle, and C. Edmiston, *J. Chem. Phys.*, **59**, 3020 (1973).
- (28) P. A. Christiansen and W. E. Palke, *J. Chem. Phys.*, **67**, 57 (1977).
- (29) M. B. Hall, *Inorg. Chem.*, **17**, 2261 (1978).

SCF MO Calculations of Nitromethane and Nitromethyl Anion

Joseph R. Murdoch,*^{1a} Andrew Streitwieser, Jr.,*^{1b} and Sam Gabriel^{1b}

Contribution from the Department of Chemistry, University of California, Los Angeles, California 90024, and the Department of Chemistry, University of California, Berkeley, California 94720. Received February 3, 1978

Abstract: Ab initio SCF MO calculations with Pople's 4.31 basis set predict a planar structure as the most stable form of nitromethyl anion and a monotonic increase in energy as the hydrogens are bent out of the molecular plane. In contrast to previous ab initio calculations, the derived structure has high C=N double bond character and N-O single bond character. Surprisingly, it is found that Pople's 4.31 basis set yields *lower* energies than Murrell's Gaussian approximation to Clementi's double ζ STO basis in spite of the fact that Murrell's basis uses *more* Gaussians. The calculated ionization potentials (Koopman's theorem) for nitromethane are in reasonable agreement with those calculated by Murrell and in fair agreement with experiment. However, previous assignments, based on semiempirical calculations, are in poor agreement with the ab initio calculations.

The structure of nitromethyl anion is of considerable interest since substituent effects on equilibria involving the anion suggest a planar, delocalized structure,^{2a} while kinetic substituent effects have been interpreted to indicate that a pyramidal carbanion may exist as an intermediate in solution proton transfer reactions of nitroalkanes.^{2b} In this paper we report ab initio SCF MO calculations on nitromethyl anion and nitromethane and examine a portion of the potential surface for distorting a planar nitromethyl anion to a pyramidal structure with HCH and HCN angles similar to nitromethane. The optimized geometries and calculated energies of nitromethane and the planar and pyramidal anions are presented in Table I.

I. Calculated Energy and Geometry of Planar Nitromethyl Anion

The calculations were performed using the program GAUSS 70³ and a 4.31 basis set.⁴ As a starting point, a planar geometry was assumed with R_{NO} (N-O bond length) = 1.228 Å, $R_{\text{C-N}}$ = 1.397 Å, $R_{\text{C-H}}$ = 1.09 Å, $\angle\text{HCH}$ = 123°, $\angle\text{ONO}$ = 121°. These parameters were those found by Murrell, Vidal, and Guest⁵ (hereafter referred to as MVG) from a minimum basis set calculation for the planar anion.

The C-H bond lengths were fixed at 1.09 Å, while R_{CN} and R_{NO} were optimized sequentially. After R_{CN} was readjusted, the ONO and HCH angles were varied, followed by reoptimization of R_{NO} and R_{CN} . The final geometry parameters and

energy were found to be R_{CN} = 1.286 Å, R_{NO} = 1.314 Å, $\angle\text{HCH}$ = 123°, $\angle\text{ONO}$ = 119°, energy = -242.691 894 au. Further variations of R_{CN} , R_{NO} , $\angle\text{HCH}$, and $\angle\text{ONO}$ indicate that the bond lengths and angles have been optimized to ± 0.005 Å and $\pm 0.5^\circ$, respectively, while the energy is estimated (parabolic interpolation) to be less than 4×10^{-5} au from the minimum. The structure we derive for the planar anion has bond lengths much closer to typical C=N and N-O bonds than the MVG structure. For example, R_{CN} for formaldoxime is 1.276 Å²⁴ compared to 1.286 Å calculated for the planar anion, while the MVG value of R_{CN} = 1.397 is significantly closer to that for nitromethane (1.489 Å).²³ The N-O bonds follow a similar pattern as seen in Table I. R_{NO} for formaldoxime is 1.408 Å²⁴ which compares to R_{NO} = 1.314 Å calculated for the planar anion, R_{NO} = 1.224 Å measured for nitromethane,²³ and R_{NO} = 1.228 Å calculated by MVG for planar anion. The 4.31 results on the optimized structure suggest that nitromethyl anion is related more closely to *aci*-nitromethane than to nitromethane itself. It is in this regard a much more reasonable structure than that calculated by MVG.

Kresge and Csizmadia have reported 3-G calculations on nitromethyl anion and a 4.31 calculation at the optimized minimum basis set (3G) geometries.¹³ The latter calculation is included in Table I. The optimized 3-G geometry of the planar anion is comparable to that found by MVG and differs substantially from the optimized structure calculated with the 4.31 basis set.