PREFACE

The force interpretation of chemical binding has received relatively little attention from chemists, in spite of the advantages inherent in such an approach. One asset is the simplification in calculation and another is the ease of interpretation, both consequences of the fact that the electronic force is determined by the real, three dimensional electron density. According to the Hellmann-Feynman theorem, the force on a nucleus in a molecule is the sum of this electronic force (which requires no integrals involving the co-ordinates of more than one electron) and the classical forces of repulsion due to the other nuclei.

Information about the nature of the binding forces in molecules is obtained in two ways. In one approach, the density in the molecule is represented by standard combinations of atomic orbitals and the resulting forces are examined. This elucidates the nature of the molecular orbitals commonly used to describe the density and hence the nature of the density itself. These results have been published in the Canadian Journal of Chemistry, 39, 1253 (1961). In the second approach the forces are assumed known and the density is required to balance these forces. The successive steps leading to

this equilibrium distribution of density contribute to an understanding of the principles of bond formation. The application of this method to the water molecule has been published in the Canadian Journal of Chemistry, 41, 586 (1963), to which journal the work on hydrogen fluoride has been submitted. A treatment of the ammonia molecule has been accepted for publication by the Journal of Chemical Physics.

I wish to record my gratitude to the many people who have contributed to the completion of the present work. The lure of quantum chemistry was first exposed to me in the stimulating approach of Professor E.G. Prout, of Rhodes University, South Africa. His encouragement and advice was greatly appreciated. I would like to thank the Canadian Commonwealth Scholarship Board for their financial assistance over the last three years and for making this visit to Canada possible. The members of the External Aid Department have been extremely helpful in their personal assistance.

I wish to extend my sincere thanks to my research supervisor, Professor R.F.W. Bader, for his willingness to discuss any and every problem and for the approach he brings to these problems. His enthusiasm and originality have been the source and mainstay of this work.

The co-operation of Professors A.B.F. Duncan, L. Salem, W.J. Orville-Thomas, T.P. Das and T. Ghose and M. Karplus in furnishing numerical information required to check or perform certain calculations is appreciated, as is the interest shown in the method by Professors C.A. Coulson and E.B. Wilson. The members of the Computing Centre of the University of Ottawa have provided valuable assistance in the computing work undertaken. Special thanks are due to Miss O. Boshko for her analysis and assistance with the three-centre integral problem, and to Mrs. D. Toop for general assistance throughout the course of this work. The use of the I.B.M. 650 machine is gratefully acknowledged. I would like to thank Mr. G. Chaton for the careful drafting of the density contour maps and other diagrams.

I am grateful to my sister Judith for her moral and technical support in the preparation of this thesis. Finally, to my fiance Peter, I dedicate this thesis with love and gratitude.

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GLOSSARY OF SYMBOLS EMPLOYED

Greek symbols.

α	alpha	β	beta	γ	gamma	δ	delta
ε	epsilon	ζ	zeta	θ	theta	λ	lambda
μ	mu	π	pi	ρ	rho	σ	sigma
τ	tau	υ	upsilon	ϕ	phi	χ	chi
Ψ	psi	ω	omega				

Ψ - the single determinantal electronic wave function.

ϕ_a - an atomic orbital on nucleus a.

ψ - a molecular orbital expressed as a combination of atomic orbitals.

Z_a - the charge on nucleus a.

ρ - the single particle density arising from the electronic wave function.

ζ - the orbital exponent in the analytical expression for an atomic orbital.

ls - a ls atomic orbital

$$= [\zeta^3/\pi]^{1/2} \exp.[-\zeta r].$$

h - a ls atomic orbital for the hydrogen atom.

S_1 - the overlap between two h orbitals.

s' - a 2s atomic orbital

$$= [\zeta^5/3\pi]^{1/2} r \exp.[-\zeta r].$$

s - an s' orbital orthogonal to ls

$$= [1/(1 - S^2)^{1/2}] [s' - S\ ls].$$

S_2 - the overlap between s and h.

S_2' - the overlap between s' and h.

p_σ - a 2p atomic orbital

$$= [\zeta^5/\pi]^{1/2} r \cos\theta \exp.[-\zeta r].$$

p_π - a 2p atomic orbital

$$= [\zeta^5/\pi]^{1/2} r \sin\theta \exp.[-\zeta r] \begin{Bmatrix}\cos\varphi \\ \text{or} \\ \sin\varphi\end{Bmatrix}$$

S_3 - the overlap between p_σ and h.

d_σ - a 3d atomic orbital

$$= [\zeta^7/18\pi]^{1/2} r^2 [3\cos^2\theta - 1] \exp.[-\zeta r].$$

d_π - a 3d atomic orbital

$$= [2\zeta^7/3\pi]^{1/2} r^2 \sin\theta \cos\theta \exp.[-\zeta r] \begin{Bmatrix}\cos\varphi \\ \text{or} \\ \sin\varphi\end{Bmatrix}$$

S_4 - the overlap between d_σ and h.

1 - refers to the letter ℓ and the number one. Where ambiguity may arise, a script ℓ is employed.

Notation.

The terminology conforms to that proposed by Mulliken as far as possible. The abbreviation L.C.A.O. is used to designate a linear combination of atomic orbitals, and an S.C.F. calculation refers to an energy variational calculation based on the self consistent field method.

In the presentation of certain results the floating point notation is used, i.e. 1.0 = 1 .... 51, 0.1 = 1 .... 50 and 0.01 = 1 .... 49.

ABSTRACT.

The Hellmann-Feynman theorem permits an evaluation of the forces operating on each nucleus in a quantum mechanical system once the electron density distribution is known. In the first part of this work the forces arising from different distributions of electron density in molecules are examined in a qualitative manner.

The relative strength of the molecular orbitals describing the density in the homonuclear diatomic molecules of the first row of the periodic table is discussed in terms of the clearly defined 'binding' and 'antibinding' concepts. A good correlation with the classification of bonding and antibonding orbitals is obtained when the definition is extended to ir·lude the nuclear contributions. The molecular orbitals are then termed 'net binding' and 'net antibinding'. Variations in bond strength of the homonuclear diatomic molecules are discussed within the molecular orbital and equivalent orbital notations on the basis of the force characteristics of the orbitals. The importance of using an orthogonal set of molecular orbitals is demonstrated.

The second type of molecule investigated is a hydride molecule HX, where two electrons occupy a bond orbital and two are localized on the X nucleus in a 'lone pair' orbital. The forces exerted on the proton and on the X nucleus are examined for different atomic orbital descriptions of the lone pair and bond orbital densities. It is found that large amounts of 2s - 2p atomic orbital mixing in either orbital generate unbalanced forces in the molecule. To attain the maximum binding force the bond orbital contribution from the X atom must be 2p in character and the lone pair orbital must be primarily 2s. It is proposed that this is always the case in hydride molecules with two electrons in a lone pair orbital. Applications of this hypothesis to polyatomic hydride molecules leads to an explanation of some variations in geometrical structure of XH_2 and XH_3 molecules.

The electronic structure of the molecules of hydrogen fluoride, water and ammonia is investigated in detail in the second application of the Hellmann-Feynman theorem. Use is made of the fact that a stable molecule must be in electrostatic equilibrium. The true electron density is one which exerts a force on each nucleus in a molecule just equal and opposite to the forces exerted

by the other nuclei. The best approximation to such a density is found in terms of a limited number of basis atomic orbitals. Satisfactory agreement is obtained when the resulting densities are tested by evaluation of molecular properties which can be compared to experimental values.

The characteristics of the electron densities satisfying the conditions of electrostatic equilibrium are those arrived at from qualitative considerations of binding force - little lone pair hybridization and bonds with the maximum possible amount of 2p character. In the two polyatomic molecules the final hybridization bears no relation to the geometry of the nuclear framework, due to the density concentration between the bonds. It is shown that the best S.C.F. wave functions predict a similar charge build-up in the region between all of the nuclei. A comparison of the predicted density distributions with the Berlin binding and antibinding regions leads to the conclusion that to achieve electrostatic equilibrium, the density in the three hydride molecules considered here concentrates in that region of the molecule where it can most efficiently bind all of the nuclei simultaneously.

GENERAL INTRODUCTION.

In recent years there has been a stocktaking among workers in the field of quantum theoretical chemistry. The question has arisen - exactly what is the aim of quantum theoretical chemistry? Some workers, whom Coulson would classify as 'group I' (1) feel that it is to find the true wave function for each molecular system, or as close an approximation to it as is feasible with recent advances in mathematical and computing techniques. The results of such calculations, while capable of yielding precise estimates of molecular properties after extensive machine computation, are usually expressed as numerical coefficients which bear no relation to chemical concepts about molecules or bonds. An extreme example of this is the elaborate wave function calculated for the hydrogen molecule (2). As Coulson (1) has pointed out, the maximum number of electrons that can be treated in an accurate energy calculation is not more than ten at present, and this may be extended to twenty with the breakdown of mathematical 'bottlenecks'.(3) This leaves a vast field of chemistry untouched.

The second group of chemists is more interested in understanding the properties of molecular systems and is therefore in closer contact with the chemist in the laboratory. Accuracy is sacrificed for insight. Into

this broad category would fall the work on the valence bond and molecular orbital theories of molecular structure which has contributed to the present understanding of electronic structure. One feature common to most of these calculations is the description of the electronic wave function as a combination of a limited number of atomic orbitals describing the wave functions of the separated atoms. Another characteristic is that they are concerned primarily with the energy of molecular systems. The comprehensive work of Ransil (4) on the simple diatomic molecules could be regarded as the logical extension of this approach. He quoted his goals as (i) a more quantitative understanding of diatomic systems which may provide a basis for the understanding of larger molecules, thereby (ii) clarifying the relationship of structure to chemical processes. He performed the most general S.C.F. calculations possible with limited sets of basis orbitals, by varying both their coefficients and their exponents. It is clear from his results that reliable estimates of those energies important in chemistry, such as the dissociation energy, cannot be obtained with limited basis sets of Slater-type atomic orbitals. In all of the diatomic and hydride molecules examined by Ransil the dissociation energies were in very poor agreement with experiment, usually no more than 50%.

The predicted dipole moments were also often in considerable error.

The various methods presently being attempted to improve energy calculations all tend towards category I. As soon as several orbitals or exponents replace the doubly occupied atomic orbital many chemical definitions or concepts lose their significance. One such example, which will be discussed in the present work, is the concept of a lone pair of electrons. If the density on the proton in a hydride molecule with lone pair electrons is described by more than one analytical function the conventional 'lone pair orbital' no longer exists. An alternative definition can be proposed, but the correlation with the ordinary lone pair is then ill-defined.

An important building block in any comprehensive theory of valence is a clear description of the electron density in terms of the component atomic orbitals. One might ask whether the electron density in molecules can be adequately described by a basis set of functions which does not yield a good energy. First it is necessary to decide whether the one-electron density found from a wave function determined by the variation principle provides the best possible description of the true density, within the framework of the chosen basis set of atomic orbitals.

It is well known that the energy is determined by the six dimensional density depending on the co-ordinates of two electrons simultaneously and not by the simple three dimensional density. A variation calculation does not therefore automatically yield the best one-electron density. Karplus and Mukherji (5) have shown this to be true for the hydrogen fluoride molecule. By including additional restraints on the values of certain one-electron operators in a variation calculation for this molecule, they obtained a higher energy than that from the simple variation calculation, but a more accurate description of specific regions of the electron density. The criterion of accuracy lies in the agreement of the calculated molecular properties obtained from one-electron operators with the experimental values. Excluding angular factors, $\langle r^2 \rangle$ measures the diamagnetic contribution to the susceptibility, $\langle r \rangle$ the dipole moment, $\langle 1/r \rangle$ the diamagnetic shielding constant, $\langle 1/r^2 \rangle$ the electric field at the nuclei and $\langle 1/r^3 \rangle$ the field gradient at the nuclei as embodied in the measured quadrupole coupling constants.

One of the great advantages of the variation method is that, starting with a wave function correct to order n, the calculated energy is correct to order n^2. As Salem and Wilson (6) point out, the expectation value of any

operator which does not commute with the Hamiltonian (and therefore the electric field operator) is correct only to order n. But this means in turn that the forces arising from the one-electron density are more sensitive criteria of the density than is the energy.

This is the basis of the present approach. Rather than using the energy to investigate the qualitative and quantitative aspects of chemical binding, these phenomena are examined in terms of the electric fields at the nuclei and hence the forces exerted on the nuclei. The calculation of forces in a molecule is considerably simplified by the theorem derived independently by Feynman (7) and by Hellmann (8). The electrostatic or Hellmann-Feynman theorem was stated by Feynman as follows:

> "The force on any nucleus (considered fixed) in a system of nuclei and of electrons is just the classical electrostatic attraction exerted on the nucleus in question by the other nuclei and by the electron density distribution for all the electrons."

The requirement that the nucleus be held stationary assumes that the Born-Oppenheimer separation of nuclear and electronic motions is valid for the system under consideration. In addition, the theorem applies only to the electron density distribution obtained from the true wave function of the system. This can be seen from Feynman's derivation of

the theorem, which is based on the Schrödinger wave equation:

The energy of a molecular system is $E = \int \Psi^* H \Psi d\tau$ where the Hamiltonian H includes only the electrostatic interactions between the particles and Ψ is the normalized electronic wave function satisfying the Schrödinger wave equation $H\Psi = E\Psi$. This gives a force on nucleus α in the x direction of

$$F_{\alpha x} = -\frac{\partial E}{\partial x_\alpha}$$

$$= -\int \Psi^* \frac{\partial H}{\partial x_\alpha} \Psi \, d\tau - \int \Psi^* H \frac{\partial \Psi}{\partial x_\alpha} d\tau - \int \frac{\partial \Psi^*}{\partial x_\alpha} H \Psi \, d\tau$$

Since H is a real Hermitian operator,

$$\int \Psi^* H \frac{\partial \Psi}{\partial x_\alpha} d\tau = \int \frac{\partial \Psi}{\partial x_\alpha} H \Psi^* \, d\tau$$

and Ψ^* satisfies the Schrödinger equation $H\Psi^* = E\Psi^*$,

$$F_{\alpha x} = -\int \Psi^* \frac{\partial H}{\partial x_\alpha} \Psi \, d\tau - E\left[\int \frac{\partial \Psi^*}{\partial x_\alpha} \Psi \, d\tau + \int \Psi^* \frac{\partial \Psi}{\partial x_\alpha} d\tau\right]$$

$$= -\int \Psi^* \frac{\partial H}{\partial x_\alpha} \Psi \, d\tau - E \frac{\partial}{\partial x_\alpha} \left[\int \Psi^* . \Psi \, d\tau\right]$$

$$= -\int \Psi^* \frac{\partial H}{\partial x_\alpha} \Psi \, d\tau$$

Under certain conditions an approximate wave function can satisfy this general Hellman-Feynman theorem, by a

suitable optimization of parameters such that the terms involving the derivative of the wave function become zero. Hurley (9) first investigated these conditions in an important series of papers dealing with the electrostatic method of calculating energies. He proved that these terms become zero when all of the variable parameters are determined by the variation method. The wave functions obtained were termed 'floating functions' since the optimum position of the atomic orbital centroids was no longer necessarily situated at the nuclei. Hurley's calculations using floating functions have since been repeated (10) with more accurate integrals. For the hydrogen molecule and hydrogen molecule ion the results were disappointing, to the extent that the authors (10) were led to conclude that the introduction of floating orbitals seemed to produce an energy improvement so small as not to be worth the extra labour involved.

Hurley (9) also investigated the correlation between the energies obtained from an approximate wave function by the electrostatic method, by a method employing the virial theorem and by use of the Schrödinger wave equation. If the orbital exponents as well as the other parameters are optimized at each value of the internuclear distance, the three methods all agree. Floating functions ensure agreement

between the electrostatic and conventional methods, irrespective of whether a variable scale factor is included. Hirschfelder and Coulson (11) have examined the relationship of the Hellmann-Feynman theorem to the hypervirial theorem. This latter theorem states that $\int \Psi^* [H,W] \Psi \, d\tau = 0$ where W is an arbitrary Hermitian time-independent operator involving the co-ordinates and momenta and E and Ψ have the same significance as previously. [H,W] is the commutator of H and W, defined by [H,W] = HW-WH. If the derivative $\frac{\partial \Psi}{\partial x_a}$ is expressed as a function of W, the precise relationship being determined by the requirement that the hypervirial theorem be satisfied, then the approximate wave function simultaneously satisfies the Hellmann-Feynman theorem. The authors (11) discussed the possibility of building up an accurate potential energy curve by calculating $\frac{\partial E}{\partial R}$ for a series of internuclear distances, from a wave function chosen at each separation to satisfy the Hellmann-Feynman theorem by the application of the hypervirial criterion.

Bader (12) has demonstrated that, for simple systems, estimates of molecular energies can be obtained by the electrostatic method without floating functions which are comparable to those found from the more elaborate and time-consuming variation method. As Salem and Wilson (6)

point out, care must be exercised in the choice of a wave function used to estimate small interactions by the electrostatic method, since the energy is only correct to the same order as the initial wave function. They examined the cases of the interaction of an atom with an external field or another atom far away, where the perturbation is small.

The general problem of the stability of a wave function under a perturbation has been treated by Hall (13). If the energy is $E_\lambda = \int \Psi^*[H + \lambda P]\Psi \, d\tau$ where P is the perturbation and λ is a parameter, then the general criterion of stability is $\frac{\partial E}{\partial \lambda} = \int \Psi^* P \Psi \, d\tau = \langle P \rangle$. In order for a wave function to satisfy the Hellmann-Feynman theorem it has to be stable to the perturbation represented by a displacement of the nucleus. Hall has proved that self consistent wave functions are stable to this nuclear perturbation[1], or indeed to any one-electron perturbation. Stanton (16) has shown that Hartree-Fock wave functions do satisfy the Hellmann-Feynman theorem, in agreement with Hall's general conclusions. In the case where the wave

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1. Hurley (14) has since pointed out that self consistent wave functions also fall under the general definition of floating functions. With Coulson (14) he has shown that some apparent inconsistencies between the work of Berlin (15), Hirschfelder and Coulson (11), Hurley (9) and Hall (13) arise from different definitions of the partial derivative $\partial H/\partial R$ in different co-ordinate systems.

function is approximated by a linear combination with arbitrary coefficients of some fixed functions, Hall showed that approximate stability can be attained by the introduction into the wave function of parameters which enable it to adjust to the presence of the perturbation. For the Hellmann-Feynman theorem, these terms would correspond to an infinitesimal change of nuclear position. Hall would assess the degree of stability achieved by the success with which the parameters introduced can be used to represent the change in the wave function under the perturbation.

This brings out a point that Hurley emphasized - the fact that a wave function satisfies the Hellmann-Feynman theorem is insufficient to ensure accurate estimates of the properties. He noted that if one chose a wave function which did not vary at all with change in the nuclear configuration it would satisfy the theorem but would give absurd results for the force and energy of the system. The more flexible the form of the wave function, particularly with respect to the perturbation of interest, the more 'stable' it becomes on variation of the parameters. Hall illustrated this by showing how the calculated dipole moment for lithium hydride improves on increasing the number of basis orbitals capable of representing the distortion in an electric field.

Since the dipole moment is calculated as <z>, a wave function which is stable to the perturbation of an electric field should be used to estimate this property. Thus the criterion of stability provides a useful indication of the changes necessary in the form of an approximate wave function which is to be determined by the variation method.

In the present work the small correction terms for the forces which would compensate for the non-ideality of the density distribution are not considered. The relationship $F_{\alpha x} = - \int \Psi^* \frac{\partial H}{\partial x_\alpha} \Psi \, d\tau$ is used to calculate the force acting on nucleus α. Only the potential energy V contributes to the force since the kinetic energy is independent of the nuclear displacement co-ordinate. This permits one to write $F_{\alpha x} = - \int \Psi^* \frac{\partial V}{\partial x_\alpha} \Psi \, d\tau$. Furthermore, in a system of nuclei (α,β) and of electrons (i,j) where the potential energy is given by

$$V = \sum_{\beta \neq \alpha} V_{\alpha\beta} + \sum_{\beta,i} V_{\beta i} + \sum_{i \neq j} V_{ij}$$

the last interaction is independent of the nuclear co-ordinate x_α. The expression for the force on nucleus α therefore becomes

$$F_{\alpha x} = - \frac{\partial}{\partial x_\alpha} \sum_{\beta \neq \alpha} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} + \sum_i e \int \Psi^* \Psi \left[Z_\alpha e \frac{\partial}{\partial x_\alpha} \left(\frac{1}{r_{\alpha i}} \right) \right] d\tau$$

$$= F_{\alpha x}(n) + F_{\alpha x}(e).$$

The nuclear contribution is simply the sum of the classical repulsive forces exerted by the nuclei in the system. In $F_{\alpha x}(e)$ the term $[Z_\alpha e \frac{\partial}{\partial x_\alpha} (\frac{1}{r_{\alpha i}})]$ is the electric field in the x direction produced by nucleus α at the position of the ith electron, or alternatively it is the field at nucleus α due to the ith electron. In order to evaluate the force one requires the single-electron density, obtained by integrating the product of the electronic wave function with its complex conjugate over the co-ordinates of all the electrons save one. Thus $\rho_1 = e \int \Psi^* \Psi \, d\tau_2 d\tau_3 \ldots\ldots d\tau_n$. The total one-electron charge density for n electrons is $\rho = n\rho_1$. This simplifies the electronic contribution to

$$F_{\alpha x}(e) = - \int \rho [\frac{Z_\alpha e \cos\theta_\alpha}{r_{\alpha i}^2}] d\tau$$

where the volume element now refers to the co-ordinates of a single electron.

The Hellmann-Feynman theorem in this form, coupled with the fact that the density determining the electronic forces is a three-dimensional one amenable to physical interpretation, lends itself readily to a qualitative investigation of the nature of binding in molecules. As far back as 1939 Feynman (7) stressed the importance of forces in problems of molecular structure. He quoted the stiffness of valence bonds, the distortions in geometry

due to repulsions and attractions between atoms and the tendency of valence bonds to occur at certain definite angles to each other as examples of the type of problem in which the idea of force is paramount. Distortions in molecules arising from the presence of orbitally degenerate ground states were originally examined by Jahn and Teller (17). The energy approach to the Jahn-Teller effect has dominated most of the work in this field, perhaps because the distortions give rise to small splittings in the energy spectra which can be measured. However, by considering the forces operative in a molecule rather than the energies, Clinton and Rice (18) have demonstrated the gain in conceptual understanding of this effect. Coulson and Strauss (19) have extended their approach to some specific hydride molecules.

Present day interest and applications of the Hellmann-Feynman theorem can be traced to the novel and imaginative application of the theorem by Berlin (15). Starting with a static nuclear framework, he demonstrated how the surrounding space could be divided into 'binding' and 'antibinding' regions depending on whether a negative charge situated within the region exerted a net force binding the nuclei together or pulling them apart. His results also served to demonstrate that bond formation can be understood and discussed within a classical framework, once the electron

density distribution has been determined by quantum mechanics. The work of Hurley (9) has contributed to the force interpretation of bond formation.

In order to reach an understanding of chemical binding through an orbital description of the electron density it is natural to examine the orbital contributions to the binding or antibinding force exerted on a nucleus. This constitutes one aspect of the present work. If the density is described by a set of orthonormal, doubly occupied molecular orbitals the total force exerted on the nuclei is simply the sum of the individual orbital contributions. The binding characteristics of the different molecular orbitals can in turn be interpreted in terms of the force contributions from the component atomic orbitals. This leads to a classification of the forces into three distinct kinds, each of which reflects a different aspect of the changes that take place in the density on bond formation. Charge polarization introduces atomic forces, charge build-up leads to overlap forces and charge removal from around each nucleus gives rise to penetration forces. The relative magnitude of the forces arising from different atomic orbitals is shown to be determined primarily by the distribution in space of the density represented by the atomic orbital, relative to the inter-nuclear axis. Relating the binding power of a

molecular orbital to the magnitude of the overlap between the component atomic orbitals is found to be misleading because it does not take into account the different spatial distributions of the overlap densities. Due to their diffuse concentration about the inter-nuclear axis rather than along it, electrons in π orbitals are much less efficient than electrons in spherical s orbitals at shielding the nuclear charge. It is demonstrated that this fact has important implications in molecular structure problems involving polyatomic hydride molecules.

A further classification of binding strength is possible by taking the nuclear forces of repulsion into account. Instead of asking merely whether an electron density exerts a binding or antibinding force, one can ask whether the force it exerts is larger or smaller than the nuclear repulsion associated with its presence. In a diatomic molecule it is a straightforward matter to assign a nuclear repulsion to each molecular orbital and examine the net resulting force. The characteristics of orbitals defined in this manner are found to correspond in general to the conventional bonding description of these molecular orbitals. Where ambiguities occur, they can be understood by an examination of the force curves, which show the forces exerted on a nucleus by the different molecular orbitals as

the component atomic orbitals approach from infinite separation to form the united atom. An explanation of the variation in bond strength across the first row homonuclear diatomic molecules is presented on the basis of these net binding and antibinding concepts.

This qualitative application of the Hellmann-Feynman theorem is performed under the assumption that simple linear combinations of atomic orbitals do provide an adequate description of the density in molecules. Starting with a chosen density one examines the binding properties resulting from the distribution. Even in this qualitative approach certain combinations of atomic orbitals have to be discarded (for example, those predicting large amounts of lone pair hybridization in hydride molecules) and other combinations have to be modified, perhaps by the inclusion of orthogonalities, in order to predict reasonable forces in the systems. An alternative application of the Hellmann-Feynman theorem is investigated as the second aspect of the present work. Instead of starting with a known density and calculating the forces, one starts with the known forces in a molecule and calculates the density. The net force on each nucleus in the stable configuration of a molecule must be zero. This fact, combined with the Hellmann-Feynman theorem yields the 'known' forces which the density has to

predict, forces which must be equal and opposite to the repulsive forces operating within the nuclear framework. The basis set of atomic orbitals employed is that necessary to describe the density in the separated atoms. If certain combinations of this limited set of basis atomic orbitals can satisfy the rigorous requirements of electrostatic equilibrium it follows that they do provide an adequate description of the one-electron density distribution. This can be tested by calculating the expectation values of the other one-electron operators which can be compared to an experimentally determined property.

The method is applied to the hydride molecules, ammonia, water and hydrogen fluoride. This iso-electronic series is of considerable interest to chemists since each molecule possesses at least one lone pair of electrons. The work of Lennard-Jones, Hurley and Pople (20), Coulson (21) and several other workers has stressed the important role that such electrons can play in the determination of molecular structure and properties. These effects are most pronounced when the lone pair orbitals are strongly hybridized, i.e. have mixed 2s and 2p atomic orbital character. The forces, being sensitive to any asymmetry in the charge cloud such as that produced by hybridization, provide a good basis for answering the question of the

importance of lone pair hybridization in these molecules. Hurley (9) took a brief look at the problem of hybridization in molecules using the Hellmann-Feynman theorem and concluded that anomalous results are obtained unless excellent wave functions are used. It is felt, in view of the present results, that this conclusion was unduly pessimistic. The limited basis set of orbitals can balance all of the nuclear forces of repulsion in these hydride molecules provided that there is no significant amount of lone pair hybridization. Another characteristic of the densities predicting electrostatic equilibrium is the presence of inner shell polarization. This 1s-2p mixing is essential to balance the force on the heavy nucleus.

The numerical values of the molecular properties obtained from the electrostatic density distributions are in very satisfactory agreement with experiment. Since the density has been concentrated in such a manner that it gives rise to the correct field at each nucleus, the resulting field gradient and potential at the nuclei as measured by the quadrupole coupling constant and diamagnetic shielding constant are evidently close to the correct values. In addition, all of the densities have either the correct dipole moment by constraint or, in one case, a slightly high dipole moment by prediction. This fact, coupled with the force criterion, ensures a good description of

the density in the region of the proton which is important in determining the susceptibility. Another important parameter affecting these molecular properties is the orbital exponent describing the density around the proton. An empirical rule is used to estimate this quantity and the results in general lend support to this method of estimating the orbital exponent.

Hence the conclusion is reached that a good description of the electron density in simple hydride molecules is attainable in terms of a limited set of atomic orbitals; and that within this framework, there can be no lone pair hybridization if the molecules are to attain electrostatic equilibrium. The maximum concentration of density in each molecule occurs in that region which would be classified binding with respect to all the nuclei in a Berlin diagram. It is demonstrated that the forces do provide a sensitive criterion of the density distribution. Just as important, the forces also provide a meaningful criterion. An examination of the force components in the molecular orbitals of hydride and homonuclear diatomic molecules leads to an understanding of some important factors determining bond strengths and molecular geometry; where these factors were previously known, a force interpretation based on clearly defined concepts is helpful in clarifying the underlying ideas.

I. A QUALITATIVE INVESTIGATION INTO THE NATURE OF BINDING IN SIMPLE HOMONUCLEAR DIATOMIC MOLECULES AND HYDRIDE MOLECULES.

I. INTRODUCTION

The Hellmann-Feynman theorem relates the forces acting on a nucleus in a molecule to the classical electrostatic forces exerted on the nucleus by the other nuclei and by the particular distribution of electrons found in the molecule. This relationship[1] may be expressed as

$$F_{\alpha x} = \frac{\partial}{\partial x_\alpha}\left[\sum_{\beta \neq \alpha} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}}\right] + \int\left[\frac{Z_\alpha e \cos\theta_\alpha}{r_{\alpha i}^2}\right] \rho \, d\tau \qquad (1)$$

where ρ is the electron density, Z_α and Z_β are the nuclear charges of atoms α and β and $[-Z_\alpha e \cos\theta_\alpha / r_{\alpha i}^2]$ is the electric field produced by the nucleus α in the x direction at the position of the ith electron.

By choosing suitable expressions for the molecular orbitals ψ_i one may calculate the force exerted on a nucleus. When the molecular orbitals used in the description of the electronic structure are all orthonormal, the electron density may be expressed in atomic units as

$$\rho = \sum_i n_i \, \psi_i^* \psi_i$$

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1. The sign convention adopted here will be adhered to throughout the ensuing work for the sake of convenience. A repulsive force on nucleus α due to another nucleus is thus negative and an attractive force is positive.

where the summation is over all of the occupied molecular orbitals and n_i (=1 or 2) is the occupation number. If F_i is taken to represent the force on nucleus α due to a pair of electrons in the ith molecular orbital, the total force in atomic units[1] may be written

$$F_{\alpha x} = \frac{\partial}{\partial x_\alpha} \left[\sum_{\beta \neq \alpha} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \right] + \sum_i \frac{n_i}{2} F_i \qquad [2]$$

Thus the contribution from each molecular orbital can be examined separately in order to classify the binding or antibinding character of the electrons occupying the orbital.

If the molecular orbitals are approximated by linear combinations of atomic orbitals (which shall be designated the L.C.A.O. approach) the electron density appears as a sum of atomic populations, centred on the two nuclei, and an overlap population due to the finite overlap of the atomic orbitals on the two centres. The force on nucleus α may be interpreted in terms of the interaction of an ideal dipole centred on the nucleus with the various atomic and overlap charge distributions. The nature of such an interaction obviously depends strongly on the position of the charge density. Three distinct

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1. One atomic unit of force is defined as $e^2/a_o^2 = 8.2377 \times 10^{-3}$ dynes. The electronic charge is e and a_o is the Bohr radius.

force contributions appear:

Atomic forces, due to density on nucleus α which is not centrosymmetric. Even small amounts of hybridization and polarization of the electron density give rise to large atomic forces on the nucleus because of the resulting asymmetry in the charge cloud around the nucleus. This same density contributes an atomic dipole to the molecular dipole moment.

Penetration forces, due to density on nucleus β. The magnitude of the force depends on the depth of penetration by nucleus α into the atomic orbital charge clouds surrounding nucleus β. This penetration effect results in imperfect screening of nucleus β and, if no other effects were operative, it would give rise to a resultant repulsive force between the two nuclei. It will be shown that the relative efficiency of different atomic orbitals in screening the nucleus, as evidenced by their penetration forces at the same internuclear distance, is an important factor determining the geometry of polyatomic molecules.

Overlap forces, due to the overlap charge distribution. This force depends on both the magnitude of the overlap and the position of this charge density relative to the nuclei. Neglect of either of these two factors can lead to erroneous conclusions about the

binding power of the overlap density. This can be seen clearly from the ideas of Berlin (15), which are outlined below.

Consider an element of charge which is placed at any point within the two full curves in the field of two nuclei of equal charge in Figure 1(a). It is evident that the net force in the x direction which this element of charge exerts on the nuclei is one which draws them together. A similar element of charge placed at a point outside the two curves (at either end of the molecule) produces an unbalanced resultant force in the x direction, one that tends to increase the internuclear distance. There will also be positions from which the forces exerted on the nuclei will be equal. These positions lie upon two boundary curves which divide the 'binding' region from the 'antibinding' regions. Diagram 1(b) shows how the antibinding region contracts near the proton and expands around the heavy nucleus in a hydride molecule. In general, it can be seen that the position at which charge is concentrated in the formation of a molecular orbital is of the utmost importance.

An investigation of the relative magnitude of orbital forces shows which molecular orbitals are the most effective (or ineffective) at binding the nuclei. An insight into why they have distinct binding properties is

then obtained from an examination of the three components - the penetration, overlap and atomic forces.

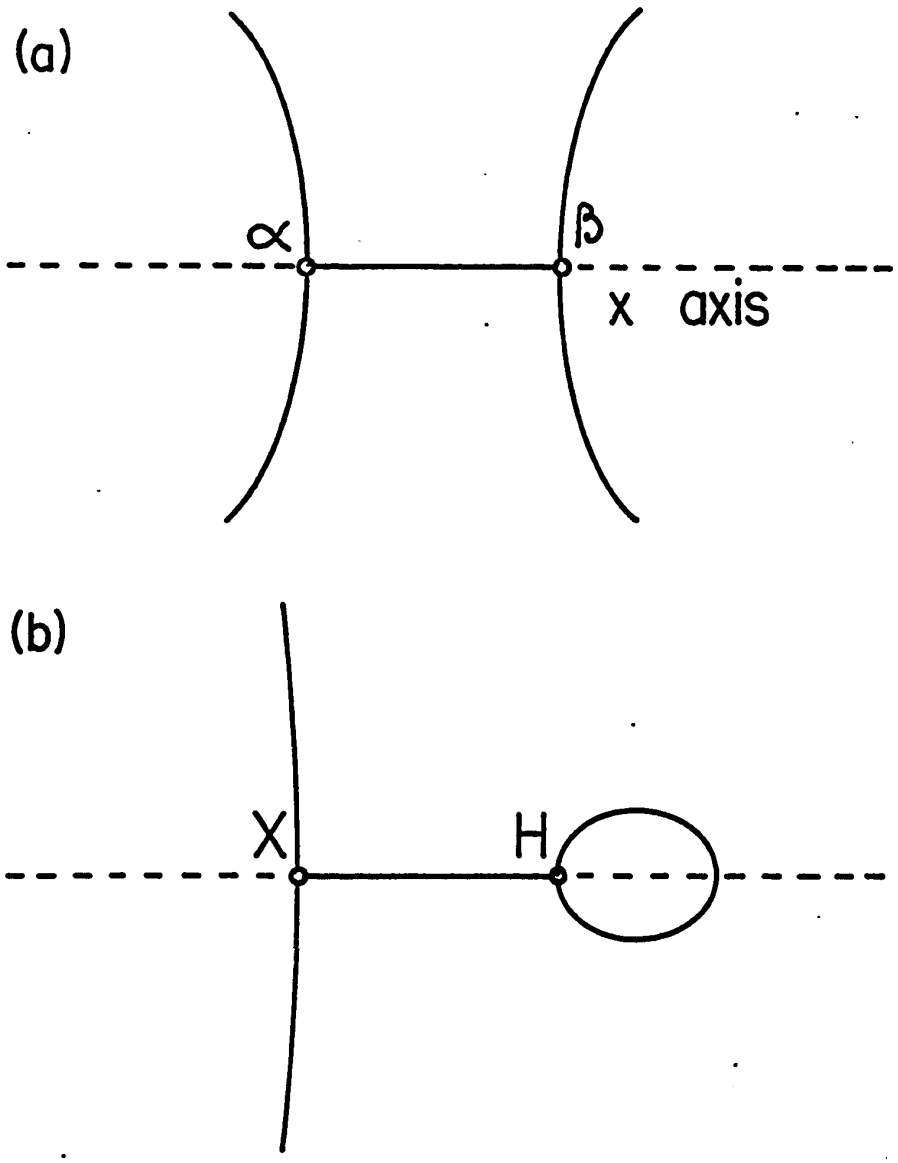

FIGURE 1. The binding and antibinding regions in (a) a homonuclear diatomic molecule and (b) a hydride molecule HX, according to Berlin.

II. HOMONUCLEAR DIATOMIC MOLECULES

General force curves.

The molecular orbitals for a homonuclear diatomic molecule are approximated by linear combinations of the atomic orbitals situated on the two nuclei α and β. They can therefore be expressed as

$$\psi_i = N_i(\phi_\alpha \pm \phi_\beta).$$

The plus sign represents a bonding combination and the minus sign an antibonding one. N_i is the normalizing factor. The electron density for the ith molecular orbital is

$$\psi_i^* \psi_i = N_i^2(\phi_\alpha^2 + \phi_\beta^2 \pm 2\phi_\alpha\phi_\beta) \qquad [3]$$

which exerts a force on nucleus α (for double occupation of a molecular orbital) of

$$F_i = \frac{Z_\alpha}{1 \pm S}\left[\int \mathcal{D}_{\alpha x}\phi_\beta^2 d\tau \pm 2\int \mathcal{D}_{\alpha x}\phi_\alpha\phi_\beta d\tau\right] \qquad [4]$$

The force due to ϕ_α^2 is zero in this case because of its symmetry about nucleus α. $\mathcal{D}_{\alpha x}$, the 'ideal dipole', is equal to $\cos\theta_\alpha / r_{\alpha j}^2$ and S is the overlap $\int \phi_\alpha\phi_\beta d\tau$. Both of the integrals in equation [4] can be expressed as a product of $(1/R^2)$ with a function of ζR. R is the bond length and ζ refers to the orbital exponent of the atomic

orbitals. The product ζR is labelled Q for convenience. (In the case of heteronuclear molecules the integrals become the product of $(1/R^2)$ with a function of Q_α and Q_β.)

Since the nuclear repulsion is $Z_\alpha Z_\beta \times (1/R^2)$ for a diatomic molecule, all the forces can be examined to advantage without the common factor of $(1/R^2)$. This requires the definition of a new 'force',

$$f_i = \frac{R^2 F_i}{Z\alpha} = \frac{1}{1 \pm S} \left[R^2 \int \mathcal{D}_{\alpha x} \phi_\beta^2 d\tau \pm 2 R^2 \int \mathcal{D}_{\alpha x} \phi_\alpha \phi_\beta d\tau \right] \quad (5)$$

which, in view of the previous discussion on the nature of the two force contributions, can be abbreviated[1] to

$$f_i = \frac{1}{1 \pm S} \left[P_\alpha(\phi_\beta, \phi_\beta) \pm 2\, O_\alpha(\phi_\alpha, \phi_\beta). \right] \quad (6)$$

It is instructive to consider the components of a typical f_i curve separately. The variation of the two forces and the overlap with internuclear distance is shown in Figure 2, for the bonding molecular orbital composed of Slater 2s atomic orbitals. For the purposes of discussion ζ can be assigned the arbitrary value of unity so that Q=R.

As R decreases the penetration force falls steadily from unity in the separated atoms to zero in the united atom. In these units the nuclear repulsion is

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1. For convenience the penetration and overlap force components defined here are dimensionless, i.e. in units of $1/R^2$.

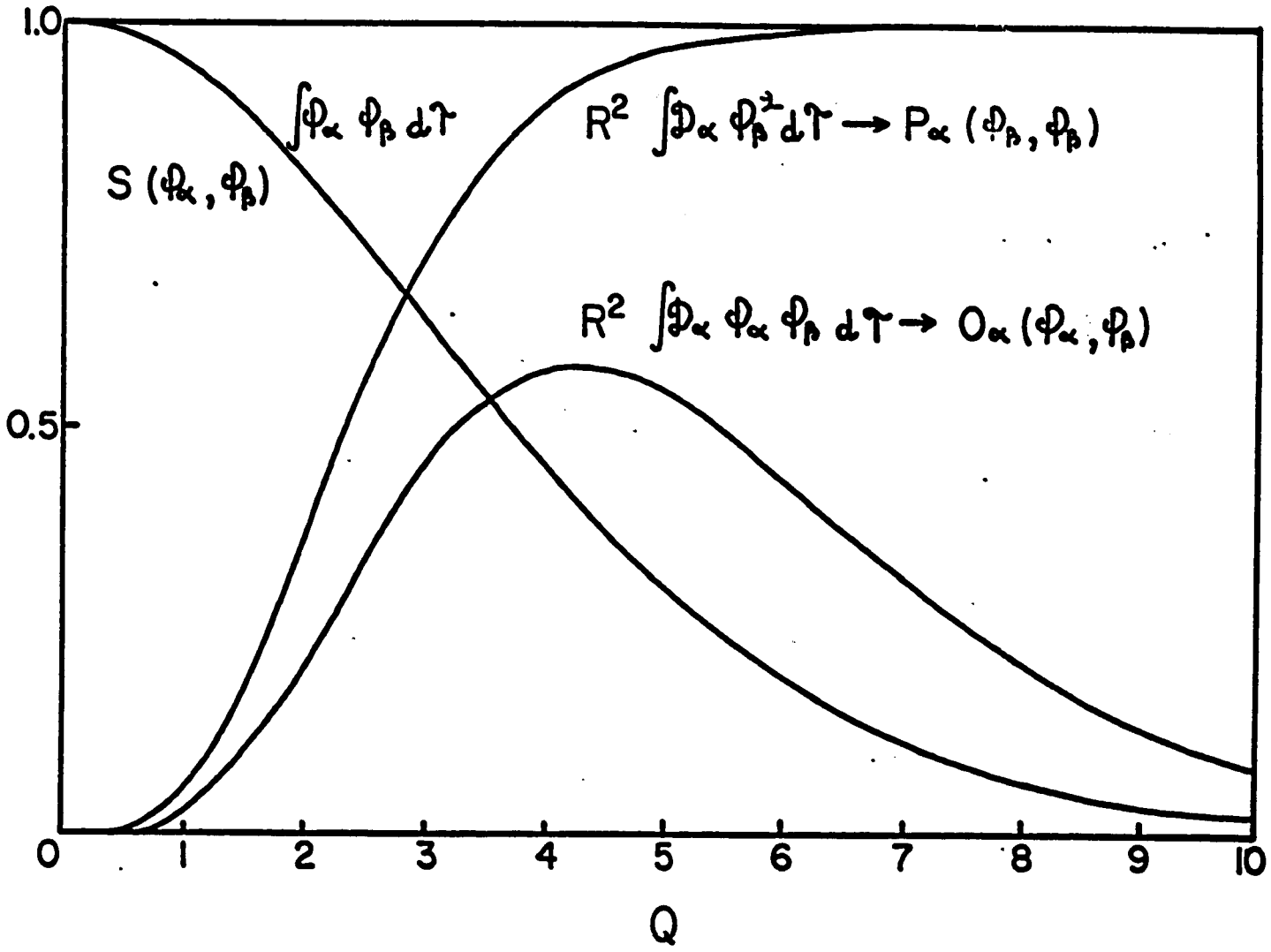

FIGURE 2. The overlap integral and the penetration and overlap force components in the $\sigma_g 2s$ molecular orbital in units of $1/R^2$ as a function of the internuclear distance. The quantity Q equals ζR, so for ζ equal to unity Q is equal to R, the internuclear distance.

simply -1 for a pair of electrons. Thus for large values of R the screening is complete[1] and the net force is zero; but as R is decreased, penetration of the charge clouds by the nuclei occurs, leading to a net repulsive force. This is counteracted by a force arising from a charge build-up between the nuclei. It is well known that the total charge transferred, $2S/(1+S)$, in a bonding molecular orbital is concentrated between the nuclei (22) and therefore primarily in the binding region. As the orbitals begin to overlap the force due to the overlap density initially increases at the same rate as the overlap S. But as the nuclei move still closer, much of the overlap charge occurs in the antibinding region and the force decreases.[2] In the limit of the united atom, where overlap is complete, the force becomes zero by symmetry. This illustrates one danger inherent in a correlation of binding force with the overlap S. The atomic orbitals constituting a <u>particular</u> molecular orbital may have a larger overlap in molecule A than in molecule B, but part of this overlap may be in the antibinding region resulting in a smaller force for molecule A.

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1. This is only true for s functions; p orbitals give rise to small quadrupolar forces at large internuclear distances.

2. This effect has been discussed by Slater (23) who illustrated it by plotting the wave functions for $\sigma_g 1s$ and $\pi_u 1s$ molecular orbitals at various internuclear separations.

There appears to be even less of a basis for correlating the binding strength of different molecular orbitals with the overlaps of their component atomic orbitals. Consider, for example, the f_i curves of the bonding molecular orbitals $\sigma_g 2s$ and $\pi_u 2p$ shown in Figure 3. Obviously the π orbital is much less binding than is the σ orbital, although its overlap S is only slightly less for any value of Q. A consideration of the forces involved illustrates why this occurs. First, a comparison of the penetration integrals $P_\alpha(p_\pi, p_\pi)$ and $P_\alpha(2s,2s)$ shows that a π orbital is much less effective at screening the nucleus than is the spherical 2s orbital. In addition the $\pi_u 2p$ orbital, while possessing appreciable overlap and transferring a considerable amount of charge to the binding region, places most of the charge above and below the internuclear axis. The maximum force from the overlap density is obtained when the charge is concentrated along the axis, for then the interaction with the nuclear 'dipole' will be a maximum. For this reason the $\sigma_g 2s$ orbital is more binding than the $\pi_u 2p$ molecular orbital, but much less binding than the $\sigma_g 2p$, shown in Figure 5 before orthogonalities are taken into account. A p_σ atomic orbital has a penetration force greater than unity due to its favourable distribution of density along the bond axis. The combination of a large penetration and overlap force

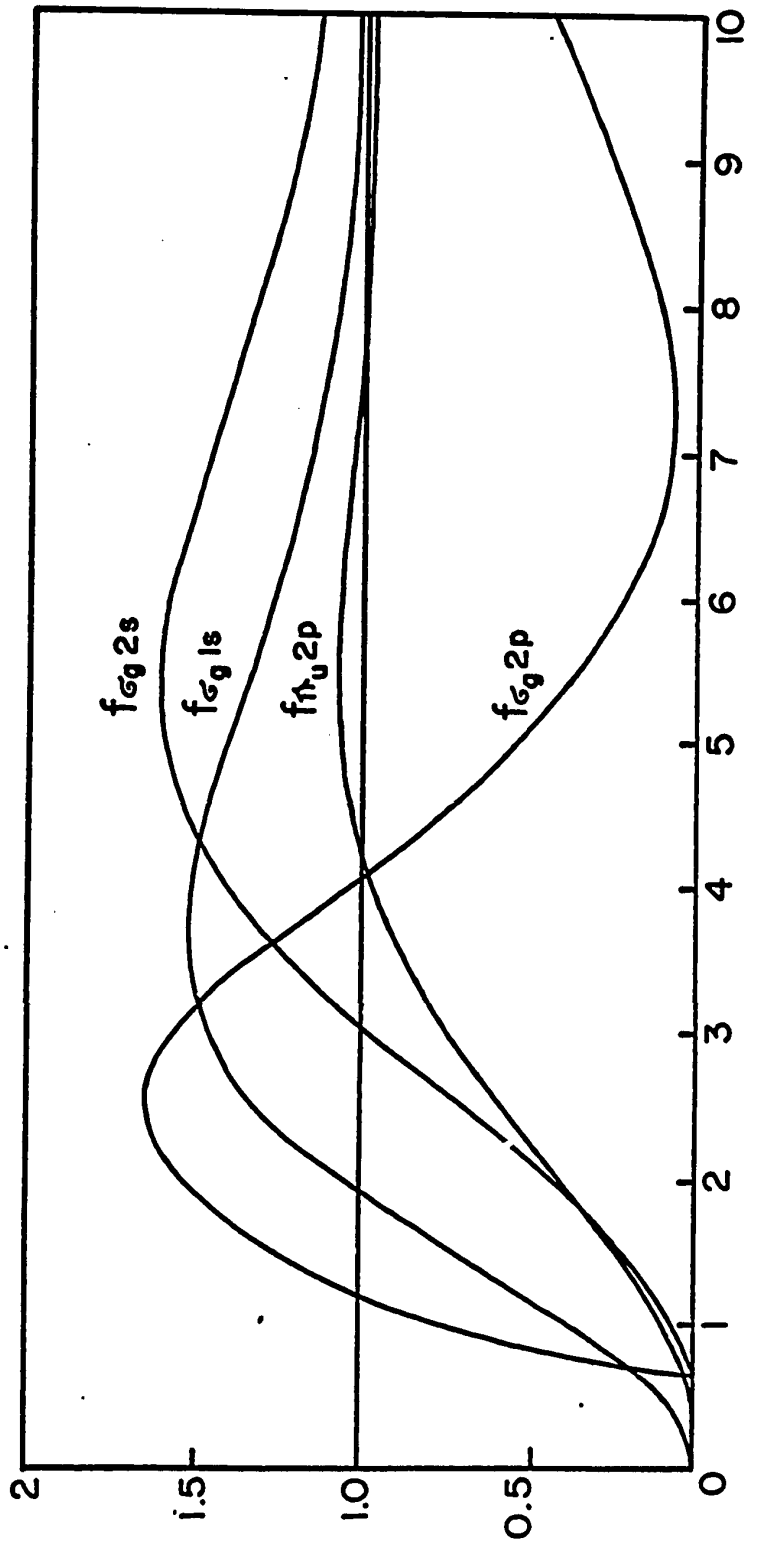

FIGURE 3. The forces in units of $1/R^2$ due to the bonding combinations $\sigma_g 1s$, $\sigma_g 2s$, $\sigma_g 2p$ and $\pi_u 2p$ (where $\sigma_g 2p$ is orthogonal to $\sigma_g 2s$) as a function of the internuclear distance.

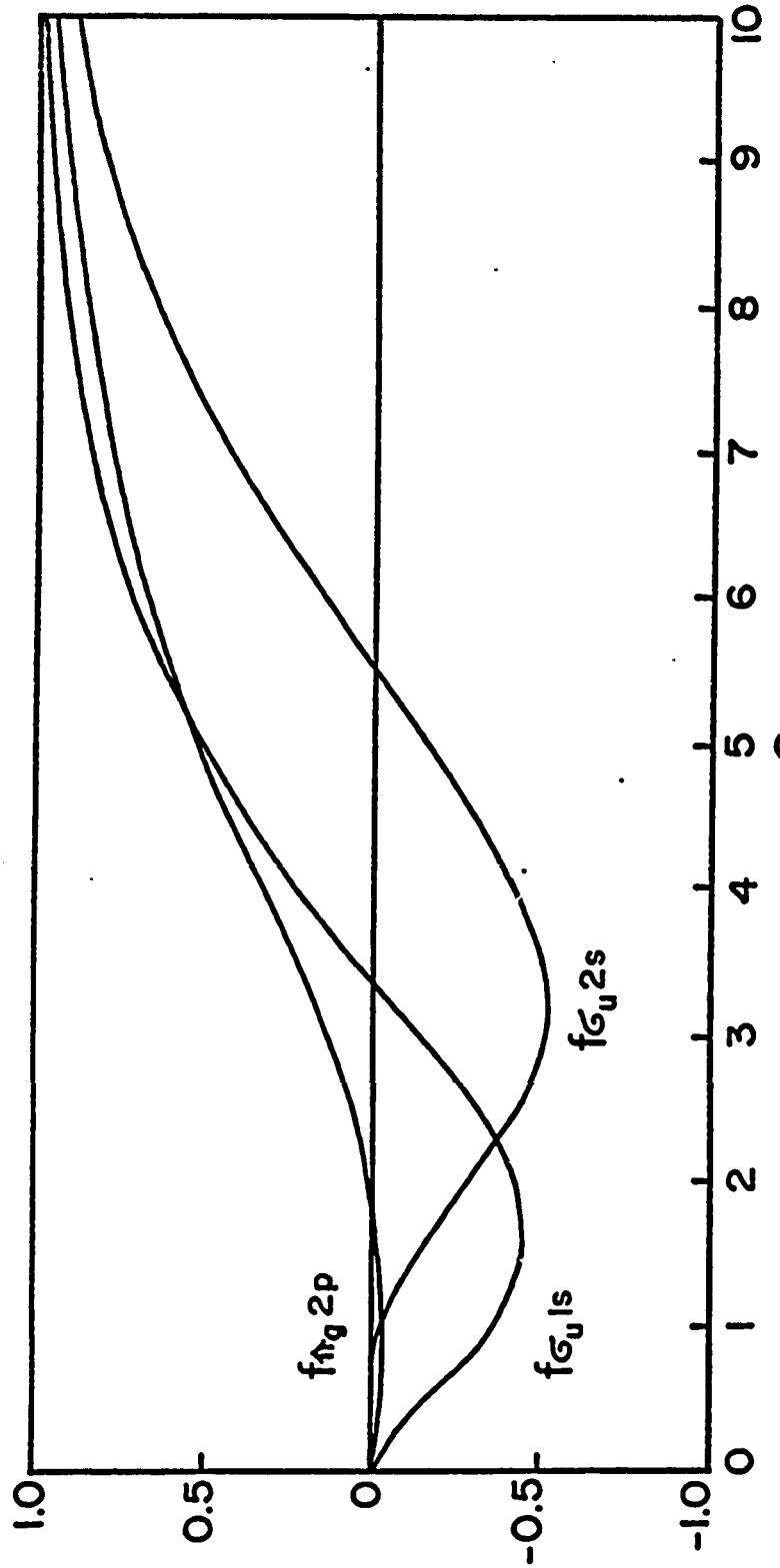

FIGURE 4. The forces in units of $1/R^2$ due to the antibonding combinations $\sigma_u 1s$, $\sigma_u 2s$ and $\pi_g 2p$ as a function of the internuclear distance.

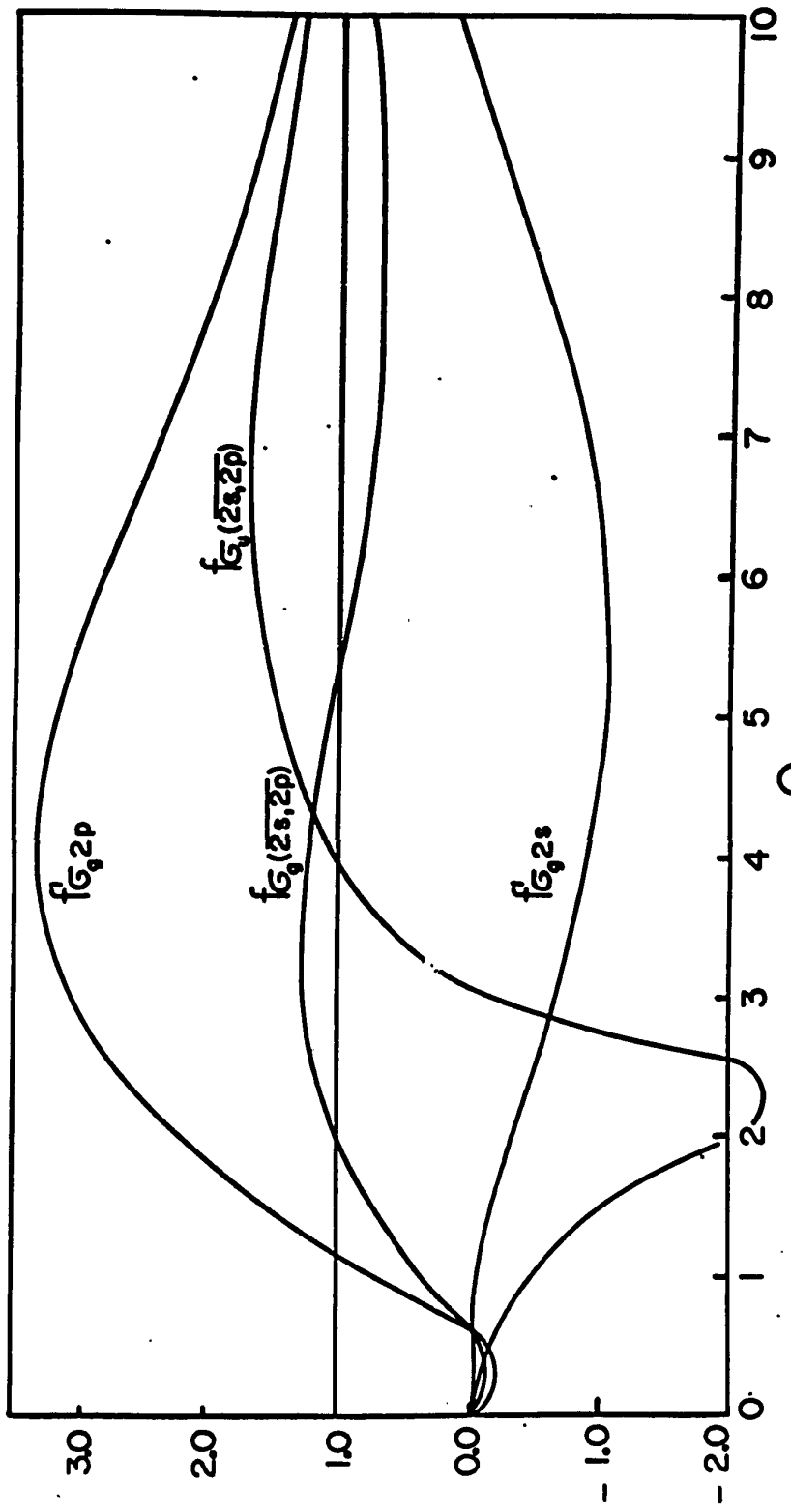

FIGURE 5. The forces in units of $1/R^2$ due to the σ 2p and orthogonal σ 2s molecular orbitals. Also shown are the forces due to the average electron densities of the mutually orthogonal pairs $\sigma_g 2s$, $\sigma_g 2p$ and $\pi_u 2s$ and $\pi_u 2p$.

makes the simple $\sigma_g 2p$ molecular orbital almost twice as effective as the $\sigma_g 2s$ at binding, in spite of its having a smaller overlap.

Exactly the same factors which operate to make a bonding combination effective at binding the nuclei together, make the antibonding combination more antibinding. Thus the $\sigma_u 2p$ (not shown) exerts by far the largest antibinding force, followed by the $\sigma_u 2s$ and then the $\pi_g 2p$. The g and u combinations of the 1s atomic orbitals behave in a manner analagous to the corresponding 2s combinations but reach their maxima and minima at smaller Q values. However, in the present discussions Q for these inner shell electrons is of such a magnitude that both 1s combinations exert a force of unity.

Effect of orthogonality on the forces.

It is easier to investigate the effect of orthogonalization on the forces than on the energies. If the molecular orbital σ_2 is made orthogonal to another molecular orbital σ_1 of the same symmetry, the resulting electron density is

$$\rho = [\sigma_2^2 + S_{12}^2\sigma_1^2 - 2 S_{12}\sigma_1\sigma_2] / (1-S_{12}^2)$$

where S_{12} is the overlap between σ_1 and σ_2. The amount of

density subtracted, $2 S_{12}\sigma_1\sigma_2$, from the original density σ_2^2 is greater than the amount added, $S_{12}^2\sigma_1^2$, since S_{12} is less than one. The orthogonalization diminishes ρ in a bonding orbital and hence reduces the force. If σ_1 and σ_2 form an antibonding combination the correction $S_{12}\sigma_1\sigma_2$ is itself negative in sign and both corrections to σ_2 are positive. In an antibonding orbital the electron density, and therefore the force, increases.

The effect on the forces of such orthogonalizations is shown in the f_i curves. In Figure 3 the $f_{\sigma g2p}$ curve is that for a $\sigma_g 2p$ molecular orbital which has been made orthogonal to the $\sigma_g 2s$ molecular orbital. The non-orthogonal $\sigma_g 2p$, shown as $f'_{\sigma g2p}$ in Figure 5, is seen to exert a force of such a magnitude as to make every other force operative in the molecule unimportant. On inclusion of the $\sigma_g 2s$ orthogonality this force decreases to a comparable value. Alternatively one can reverse the roles of the two molecular orbitals in the orthogonalization procedure. In Figure 5 it can be seen that $f'_{\sigma g2s}$ is now much less binding than is $f'_{\sigma g2p}$. Thus it is rather arbitrary to speak of the relative binding properties of the $\sigma_g 2s$ and $\sigma_g 2p$ molecular orbitals in a molecule. When both of these orbitals are occupied there will be some resultant force from those orbitals of principal quantum number two with σ_g symmetry. This total force is plotted

in Figure 5 for the bonding and antibonding combinations. The average of the $f_{\sigma g2s}$ and the orthogonal $f_{\sigma g2p}$ (or equally well, the average of the $f'_{\sigma g2s}$ and $f'_{\sigma g2p}$ curves) is denoted by $f_{\sigma g(\overline{2s,2p})}$ and the average of the values obtained from the orthogonal $\sigma_u 2s$ and $\sigma_u 2p$ orbitals is called $f_{\sigma_u(\overline{2s,2p})}$. It can be seen that at large values of Q the average contribution from the bonding orbitals is actually less binding than that from the antibonding orbitals. Whether or not this is a real effect could only be decided on inclusion of the appropriate 1s orthogonal molecular orbitals, a contribution neglected here for the sake of simplicity, but necessary in a detailed application of the electrostatic method to a particular molecule.

By consideration of the forces one brings into sharp focus the fact that the concept of a molecular electronic configuration in terms of molecular orbitals does have definite limitations. The order of the orbital forces is at the complete mercy of the orthogonalization procedure and has no real significance. All that does possess ultimate significance is the total force for a molecule, not how this force is divided into contributions for the different orbitals.

In general, the f_i curves illustrate that for any value of Q, the process of orthogonalization reduces

both the binding properties of bonding orbitals and the antibinding properties of antibonding orbitals. Mulliken (24), from qualitative considerations of overlap integrals, has stated that the effect of this 'forced hybridization' is "to weaken very considerably the bonding power of bonding molecular orbitals but to strengthen markedly the antibonding power of antibonding molecular orbitals." The present results therefore disagree with Mulliken's predictions concerning the effects of forced hybridization on the antibonding orbitals.

Binding character of molecular orbitals.

Much of what has been written about the bonding character of molecular orbitals is based on spectroscopic observation. As Coulson (25) pointed out, such an observation serves as a definition of an antibonding electron. Nevertheless much more is inferred from the results of such an observation, namely that the electron when present in the molecule actually did exert an anti-binding force. It can be demonstrated that this is rarely the case.

The electrostatic calculations allow for a clear definition of an antibinding and binding molecular orbital. The force curves f_i give immediately the net force due to any particular density distribution. The obvious definition of a binding orbital is one for which f_i is positive at the particular Q which is of interest; and of an antibinding orbital, is one for which the pertinent value of f_i is negative. A negative value of f_i implies that the electrons are distributed in such a fashion as to draw the nuclei apart, which is the simplest interpretation of an antibinding electron. Reference to Figure 4 illustrates that the antibonding orbitals possess negative f_i values only for very small values of Q, corresponding to a very close approach of the atoms to distances usually less than R_e. This indicates that at the equilibrium distances in molecules the charge transferred, 2S/(1-S), in antibonding orbitals is still placed primarily in the binding region. Only when the nuclei approach more closely does the amount of charge in the antibinding region outweigh that in the binding region. Reference to equation (6) shows that the analytical requirement for antibinding is for $2\rho_a(\phi_a,\phi_\beta) > P_a(\phi_\beta,\phi_\beta)$.

A further classification of binding power is possible which is useful in the interpretation of bond

strengths. At large values of Q all of the f_i curves tend towards unity as the total force approaches zero. As Q decreases, the bonding orbitals show an increase above unity while the antibonding orbitals possess f_i values which drop steadily below unity, eventually reaching negative values at small Q. Because of this it is of interest to express the total force as

$$F_{ax} = \frac{Z_a}{R^2} \times \sum_{i}^{n} (f_i - 1) \text{ where } n = Z_a. \qquad [7]$$

When written in this form it can be seen immediately how effective the molecular orbitals are at shielding the nuclear charge. If (f_i-1) is negative it implies that the two electrons in the ith molecular orbital are distributed in such a way that the resulting density concentration is inadequate to screen their share of the nuclear charge. Their presence contributes a resultant repulsive force to the molecular system so this orbital is termed <u>net anti-binding</u>. When (f_i-1) is positive the electrons not only provide the shielding amount of force, but exceed this by a favourable transfer of charge into the binding region. Such a molecular orbital is termed <u>net binding</u>.

Reference to Figures 3 and 4 illustrates that these definitions coincide with the usual assignment of antibonding and bonding properties of the molecular

orbitals. For instance, the π_g molecular orbital is net antibinding and is classified as antibonding from its form, $N(\pi_\alpha - \pi_\beta)$. A consideration of its force curve in Figure 4 throws light on the apparent anomaly that when an electron is removed from the π_g orbital in carbon dioxide the bond length increases, but in oxygen the resulting ion has a shorter bond length (26). The same orbital, antibonding in form, must be classified as bonding in one situation and antibonding in the other according to the spectroscopic definition.

The major difference in the molecular orbital for the two cases lies in the Q values. The oxygen 2p orbital exponents (as given by an empirical rule which will be discussed in Part II) are 2.28 in carbon dioxide and 2.12 in oxygen, but the O-O distance is much greater in carbon dioxide than it is in oxygen. This leads to a Q of 10 in carbon dioxide compared to 4.8 in oxygen. Figure 4 illustrates that the π_g electrons are barely net antibinding at Q=10 but quite strongly so at Q=5. On removal of such an electron the effective nuclear charge for the remaining electrons increases at the same value of R, resulting in a larger Q and therefore force/electron. Whether this increase can compensate for the loss of binding force depends on the region of the force curve. Around Q=10 the force is changing very slowly so that the

net increase in force/electron in carbon dioxide is small. The nuclei are therefore pulled apart until equilibrium is restored. Around Q=5 the forces are changing very rapidly and, in addition, the binding force lost by the removal of the electron is only one-half of the force lost at Q=10. It can readily be understood that the single π_g electron, with an increased Q value, exerts a larger force on the nuclei at the same value of R than did both electrons. The nuclei therefore move together until a new equilibrium position is attained. Associated with this change in nuclear position will be a rearrangement of the other molecular orbitals leading to stronger bonding at the smaller bond distance in the O_2^+ ion. This interpretation is analagous to that proposed by Moffit (27) for the change in bond length of carbon dioxide. He suggested that the residual electron distribution rearranges in such a way that the bond order decreases. This explanation was put forward as an alternative to that of Mulliken (28), who considered that the apparent bonding character of this π_g orbital must be due to participation of a 3d atomic orbital on carbon.

The $\sigma_g 1s$ and $\sigma_u 1s$ molecular orbitals for the homonuclear diatomic molecules from Li_2 across, all possess a value of Q>10 at R_e. The quantity $(f_i-1) = 0$,

which implies that electrons in these molecular orbitals exactly shield the corresponding nuclear charge. They may therefore be classified as non-binding. The force curves illustrate that one is justified in labelling them as localized KK orbitals in the molecular orbital description of these molecules.

Variation in bond strength.

The well-known variation in bond strength across the first row diatomic homonuclear molecules can be explained in terms of the binding characteristics of the molecular orbitals. The nitrogen molecule possesses the strongest bond, as evidenced by the largest dissociation energy and shortest bond length. The six electrons of highest energy occupy the net binding orbitals, $(\sigma_g 2p)^2$ (actually containing some contribution from the other orbitals of σ_g symmetry) and $(\pi_u 2p)^4$. In the oxygen molecule the extra pair of electrons occupy the $\pi_g 2p$ orbital which is net antibinding in this case. At the same Q value as nitrogen the presence of the electrons does not counteract the additional nuclear repulsion. This results in a lengthening of the bond distance. The subsequent addition of two more net antibinding electrons in the fluorine molecule results in a still longer and weaker bond for

this molecule. Proceeding in the opposite direction from nitrogen, the bonds become weaker as net binding electrons are progressively removed from the system. Thus C_2 has one electron less than nitrogen in the $\pi_u 2p$ and in the $\sigma_g 2p$ molecular orbitals and obtains only 3/4 and 1/2 respectively of the net binding forces from these two orbitals at any value of Q. This explanation of the variation in the bond strengths of the diatomic molecules is essentially the same as that obtained from the usual interpretation (29) if one replaces the terms bonding and antibonding with the terms net binding and net antibinding. However, the present discussion is necessarily less speculative than is one based on bonding abilities deduced solely from the forms of the molecular orbitals.

An alternative but entirely equivalent description of the electron density is possible in those molecules which have doubly occupied molecular orbitals. Pople (30) has discussed the equivalent orbital approach to the first row diatomic molecules. He shows that the bonding and antibonding combinations of doubly occupied atomic orbitals can rigorously be transformed into two localized equivalent orbitals. Thus the $\sigma_g 1s$ and $\sigma_u 1s$ are equivalent to two inner shell electrons on each nucleus, the $\sigma_g 2s$ and $\sigma_u 2s$ to localized 2s electrons and the $\pi_g 2p$ and $\pi_u 2p$ to

localized $2p\pi$ electrons. In order to explain the decrease in bond strength from nitrogen to fluorine in terms of energies, it is necessary to postulate that any antibonding combination is more antibonding than is the bonding combination bonding (25); the net effect must be one of repulsion. The nature of this repulsion is immediately obvious in view of the localized or 'lone pair' description of four such electrons. The penetration force exerted on nucleus α by 2 electrons in a lone pair orbital on nucleus β decreases in the order $2p_\sigma > 1s > 2s > 2p_\pi$. For a value of Q such as that found in first row molecules, the $2p_\sigma$ electrons shield more than 2 units of nuclear charge, the 1s electrons exactly 2 units, the 2s electrons slightly less (~1.9) and the $2p\pi$ electrons considerably less (~1.5). This means that the 4 electrons in $\sigma_g 2s$ and $\sigma_u 2s$ will be net antibinding to a small extent, but the result of placing electrons in the antibonding combinations of the π orbitals is to generate a strong repulsive force in the molecule.

The equivalent orbital description of the bonds in the nitrogen molecule is one of three 'bent' bonds, obtained by combining the σ and two π bonding molecular orbitals. The only localized electrons are in s orbitals and therefore efficiently shield the respective nuclear charges. All the factors contribute to make this a strong

bond. Since the extra electrons in the oxygen molecule are in two different degenerate π molecular orbitals the equivalent orbital transformation cannot be performed. In the fluorine molecule all of the molecular orbitals are doubly occupied and so can be considered as one σ bond and four lone pair electrons of the π type on each nucleus. The four electrons that were in net binding $\pi_g 2p$ molecular orbitals in nitrogen have been replaced by eight electrons in net antibinding lone pair orbitals. The resultant antibinding force can only be overcome by an increase in the inter-nuclear distance, so that the penetration force of the π orbitals approaches closer to their nuclear repulsive force. Again it can be seen that all the factors operate to give fluorine the very weak bond it is found to possess. It is unnecessary to invoke repulsions between the lone pair electrons - by their very nature they constitute a net repulsive force within any molecule.

III. SOME HYDRIDE MOLECULES WITH LONE PAIR ELECTRONS.

In HX hydride molecules the effect of hybridization on the forces can readily be investigated. The general expression for a normalized bond orbital due to the overlap of some hybrid of s and p orbitals (orthogonal to the inner shell 1s electrons) on X with the 1s orbital on hydrogen (denoted by h) is

$$\psi_b = \lambda(\cos\varepsilon_b\ s + \sin\varepsilon_b\ p) + \mu h\ .$$

The lone pair orbital directed out behind the X atom along the bond axis is

$$\psi_l = \cos\varepsilon_l\ s - \sin\varepsilon_l\ p.$$

The ratio λ/μ measures the relative importance of the X and hydrogen contributions to the bond orbital and is termed the polarity. It is of primary importance in determining the dipole moment of the distribution. The remaining parameters ε_b and ε_l measure the bond and lone pair hybridization respectively. They are not independent: for example, as the lone pair loses p character the bond orbital must increase in p character. This is shown in a more detailed approach from the requirement of orthogonality between the two orbitals.

The forces exerted by the electrons in these orbitals will be considered separately for both nuclei.

Force on nucleus X.

In the expressions for the forces it is most convenient to denote the penetration forces by P, the

overlap forces by 0 and the atomic forces, which arise when hybridization occurs, by A. (A factor of $[1/R^2]$ is not removed from these forces.) Then the forces exerted on the X atom along the bond axis by the electron density distribution are, for the bond orbital

$$F_{bX} = \lambda^2[4 \cos\varepsilon_b \sin\varepsilon_b A(s,p)] + \mu^2[2 P(h,h)]$$

$$+ 4\lambda\mu[\cos\varepsilon_b 0(s,h) + \sin\varepsilon_b 0 (p,h)]$$

and for the lone pair orbital,

$$F_{lX} = -4 \cos\varepsilon_l \sin\varepsilon_l A(s,p).$$

In Figure 6 are plotted F_{bX} and F_{lX} as a function of their hybridization parameters, for orbitals corresponding to an O-H bond. The general form of the curves is the same for any X-H molecule. The polarity λ/μ has the value 1.00 in F_{bX}; for a slightly increased λ/μ, about 1.4, the two end points of F_{bX} drop slightly and the maximum in the curve is slightly increased. In the limit of $\lambda/\mu = \infty$, F_{bX} will equal $-F_{lX}$.

It is assumed that any other electron pairs on the X nucleus are in s or p_π orbitals and therefore exert no force on the X nucleus. Figure 6 can be applied to the series of ten electron hydrides consisting of ammonia, water and hydrogen fluoride. For each of these molecules

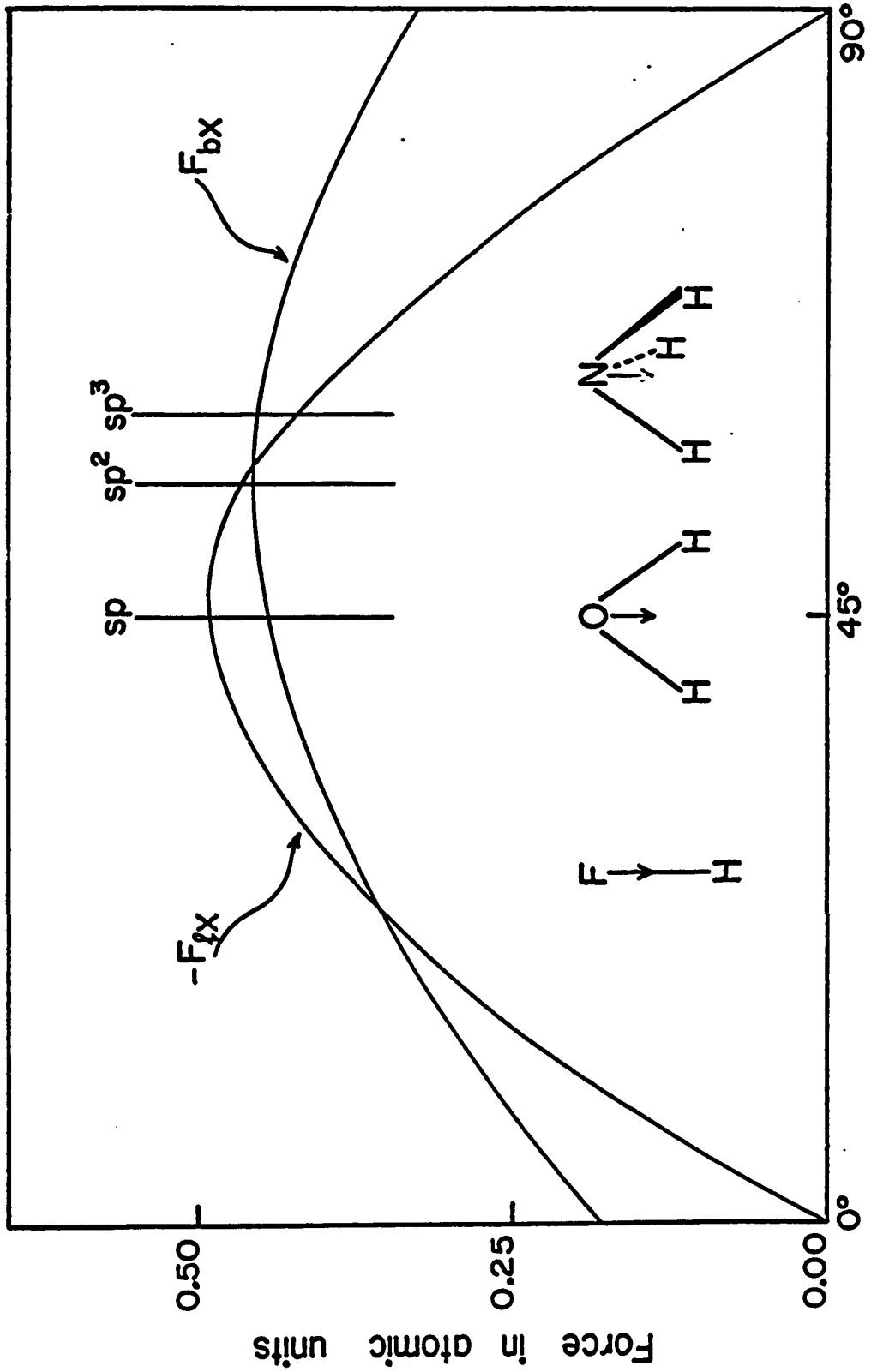

FIGURE 6. The forces exerted on the X nucleus in HX by the lone pair and bond orbital electron densities as a function of their respective hybridization parameters ϵ_l and ϵ_b.

one is interested in the resultant force on the N, O and F nuclei as indicated in Figure 6. They each have one pair of electrons which can exert a force on the heavy atom. The ammonia molecule has one lone pair orbital directed back along the symmetry axis. Its hybridization can vary from s to approximately sp^3. The two equivalent lone pair orbitals in the water molecule vary from sp to approximately sp^3. They may be considered equally well as a single p_π orbital perpendicular to the plane of the molecule and a second orbital, in the plane of the molecule and directed back along the force axis, which can vary from s to approximately sp^2. Appropriate linear combination of these two orbitals gives back the equivalent lone pair orbitals. The three lone pairs of electrons in hydrogen fluoride occupy two p_π orbitals which exert no force on the fluorine nucleus and a hybrid orbital back along the bond axis which may vary from s to p. F_{lX} therefore applies directly to all three of these molecules. F_{bX} holds strictly only for hydrogen fluoride and not the polyatomic molecules, since components of F_{bX} for each bond must be taken along the indicated force axes. New force components also appear in water and ammonia. However, it is found that the components are such that the two O-H bonds in water and the three N-H bonds in ammonia add up very close to that of a single O-H and N-H

bond respectively along the direction of the force. The general results found here therefore apply to these two molecules as well as to hydrogen fluoride.

Reference to Figure 6 shows that the lone pair electrons cannot occupy strongly hybridized orbitals if the molecules are to attain electrostatic equilibrium. The force exerted on nucleus X by the lone pair electrons is zero when they occupy either an s ($\varepsilon_1=0$) orbital or a p ($\varepsilon_1=90^o$) orbital. But hybridization results in density being removed from the binding region between the nuclei to the antibinding region behind the heavy nucleus. Since this charge transfer takes place quite close to the nucleus the magnitude of the resulting atomic force is very large. This led Hurley (9) to conclude that the contribution from this atomic force term "completely swamps the effect of all other contributions to the force acting on the fluorine nucleus in the molecules HF and F_2". If the lone pair electrons were strongly hybridized this would indeed be true. When the hybridization parameters are 45^o the lone pair electrons exert a larger antibinding force than the bond electrons exert a binding force and the net force acting on nucleus X is greater than the nuclear repulsion. While Hurley concluded that the solution lay in abandoning the orbitals in favour of ones which represented the hybridization more accurately, the present conclusion is that the hybridization has to be

abandoned in order for the orbitals to give reasonable estimates of the forces.

Whether the lone pair orbital becomes s or p depends on the relative binding strength of the p and s atomic orbitals in ψ_b. Figure 6 demonstrates that the order of forces for different bond hybridizations is $sp^2 \backsim sp \backsim sp^3 > p > s$.

The strongly hybridized orbitals exert the largest force on X, but as discussed above they cannot be utilized in bond formation since the lone pair electrons then give large atomic forces in the opposite direction. A p orbital ($\varepsilon_b=90^o$) is therefore the best compromise. This orbital concentrates charge density along the bond axis where it exerts more force than if it were spherically disposed in an s orbital. Thus $O_X(p,h)$ is almost three times larger than $O_X(s,h)$. A hybrid orbital is more effective than the p orbital alone due to the introduction of atomic force terms which provide additional binding force in the bond orbital.

In hydrogen fluoride the bond would be expected to be primarily p in character, with the lone pairs in one s and two p_π orbitals. The hybridization in water and ammonia, if determined by the molecular geometry, would fix the lone pairs at sp^2 and sp^3 respectively. It becomes necessary to postulate bent bonds in these

molecules. If the angle between the bond orbitals is approximately 90° these will be primarily p orbitals and the sigma lone pair electrons will be in s orbitals.[1]

Force on the proton.

A consideration of the forces exerted on the hydrogen nucleus by the electron density in ψ_b and ψ_l leads to an identical conclusion, i.e., that the lone pairs will be largely s and the bonds largely p. The expressions for these forces are

$$F_{bH} = 2\lambda^2[\cos^2\varepsilon_b\, P(s,s) + \sin^2\varepsilon_b\, P(p,p) + 2\cos\varepsilon_b \sin\varepsilon_b\, P(s,p)] + 4\lambda\mu[\cos\varepsilon_b\, O(h,s) + \sin\varepsilon_b O(h,p)]$$

$$F_{lH} = 2[\cos^2\varepsilon_l\, P(s,s) + \sin^2\varepsilon_l\, P(p,p) - 2\cos\varepsilon_l \sin\varepsilon_l\, P(s,p)]$$

These forces are presented in Figure 7 as a function of their hybridization parameters. In this case the contributions to F_{lH} are all of the penetration type. It is clear from the limits of this force curve that a p_σ orbital is more effective than is an s orbital at screening the X nucleus from the proton. The force exerted by the lone pair electrons undergoes a large decrease when hybridization is extreme, for density is removed from

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1. The full treatment of the molecules of water and ammonia shows that this angle is actually less than 90° when delocalization is taken into account.

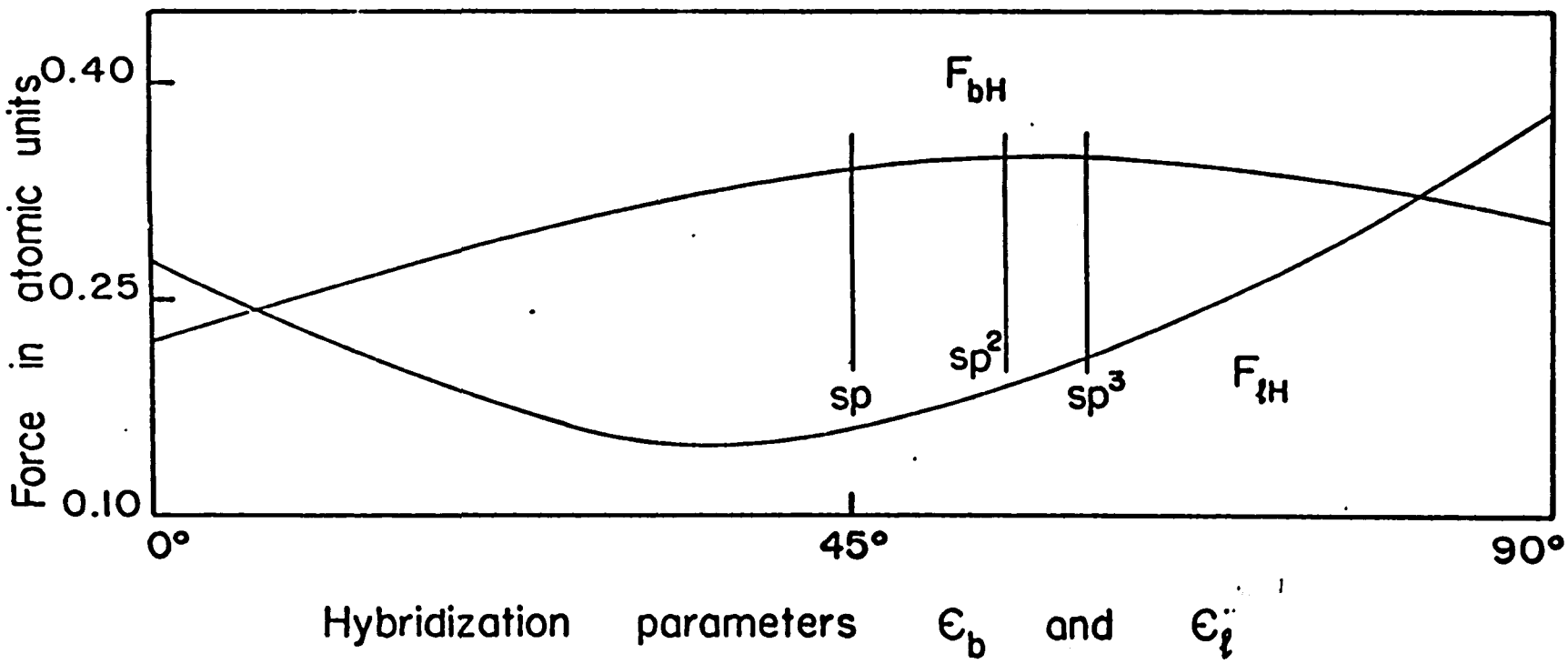

FIGURE 7. The forces exerted on the proton in HX by the lone pair and bond orbital electron densities as a function of their respective hybridization parameters ϵ_l and ϵ_b.

the hydrogen side of X and placed on the side remote from the proton. This results in a repulsive force on the hydrogen nucleus, since the lone pair electrons no longer shield their part of the nuclear charge. They become net antibinding. The forces on the proton and on nucleus X due to the density in the bond orbital exhibit the same features. The variation with hybridization of the force on the hydrogen nucleus is less pronounced due to the absence of atomic forces. The order of forces for bond hybridizations is now

$sp^3 \backsim sp^2 \backsim sp > p > s.$

This is the same as before aside from a slight reordering of the forces for large hybridization. A p bond again produces a much stronger force than that from a bond formed by an s orbital. The largest force is achieved by making the bond mainly p in character and the lone pair largely s.

A consideration of the forces exerted on the proton by all of the electrons is of use in understanding why certain hydride molecules are bent rather than linear, or pyramidal rather than planar. Consider the general expression for the electronic force exerted on a hydrogen nucleus along an O-H bond axis in the water molecule. For a linear or bent molecule this can be written as

$$F_{\parallel} = F_{b1} + F_{b2} + F_{\ell 1} + F_{\ell 2} + F_{1s}.$$

The first term is the electronic force on $H_{(1)}$ due to ψ_{b1} and the second term is that due to the density in ψ_{b2}. $F_{\ell 1}$, $F_{\ell 2}$ and F_{1s} are the forces due to the two lone pairs and the inner shell electrons. The nuclear repulsion due to oxygen can be written as $4\ (-2/R^2)$ where R is the O-H bond length. There is a small additional repulsion from the second proton. Since the inner shell electrons are tightly held around the oxygen nucleus they screen exactly two units of this nuclear charge in any nuclear configuration. One lone pair of electrons can always be left in a p_π orbital. These electrons exert a net antibinding force; they are concentrated above and below the bond axis and shield only 75% of the appropriate nuclear charge. The second lone pair of electrons occupies a $p_{\pi'}$ orbital in the linear configuration of the water molecule and consequently exerts the same antibinding force. As the bond angle is bent this orbital takes on increasing s character, reaching the limit of pure s when the orbital angle is allowed to decrease to less than the equilibrium bond angle. Electrons in the spherical s orbital shield about 95% of the corresponding nuclear charge.

The force exerted by ψ_{b1} and ψ_{b2} can be considered in relation to the remaining $-2/R^2$ units of oxygen repulsion and the small proton repulsion.

It is generally true that a bond orbital exerts a binding force, which helps to counteract the net antibinding of the p_π electrons. As the bond angle in water decreases the sp character of ψ_{b1} changes to p, which results in a small decrease in its net binding force. But simultaneously the force exerted by the density in ψ_{b2} increases as this density moves closer to $H_{(1)}$. The overall contribution from the bond orbitals hardly changes. Inclusion of the slightly increased proton repulsion probably results in a small decrease in the net binding force. Hence the reason for a bond angle of less than 180° in the water molecule can be summarised as follows: In decreasing the bond angle, the attractive force of the bond electrons for the protons remains almost constant, but the attractive force of the lone pair electrons increases significantly as the p_π orbital assumes s character and consequently shields the oxygen nucleus more efficiently.

For the same reasons the pyramidal form of ammonia is more stable than the planar form. As the hydrogen atoms move out of the plane the total force due to the bond electrons again remains constant or decreases slightly. The lone pair orbital, by changing from p_π to s, can better shield the nitrogen nucleus. A greater force of attraction on the hydrogen nucleus, and hence a more stable molecule, results. One can generalize this result

to include all hydride molecules possessing lone pair electrons:

In hydride molecules which possess at least one lone pair of electrons the bond orbitals will be primarily of p character and the lone pair orbitals will contain close to the maximum possible amount of s character.

Application of the general rule.

This rule implies that the important factor determining whether XH_2 and XH_3 molecules are bent is the presence or absence of a lone pair of electrons in a single orbital. If there are no lone pair electrons, as for example in CH_3^+ and BH_3, the maximum binding force can be attained in planar configurations where the bond orbitals are strongly hybridized. Similarly in the methane molecule the large attractive forces associated with sp^3 hybridization can be realized without a resultant imbalance of the forces exerted on either the carbon or hydrogen nuclei.

The CH_3^- ion, which is isoelectronic with ammonia, can reach its most stable configuration by assuming a pyramidal shape and thereby increase the shielding of the carbon nucleus. The singlet state of methylene with both unshared electrons in a single orbital

should also be bent. The triplet state of methylene with two unshared electrons in distinct p_π orbitals is a borderline case, as is the BH_2 molecule which has one unshared p_π electron. A firm prediction could only be made after more detailed calculations; but a comparison of the penetration forces $P_H(p_\pi, p_\pi)$ and $P_H(s,s)$ indicates that the difference between them for a single electron will not be sufficient to cause such molecules to bend. This is borne out by spectroscopic evidence that all the excited states of ammonia which arise from excitation of one lone pair electron are planar (31).

The conclusions reached here concerning the factors governing the shapes of XH_2 and XH_3 molecules are the same as the empirically based rules advanced by Walsh (32). The method and interpretation used in arriving at these conclusions is necessarily very different, since he was concerned entirely with the energy of the systems.

II. A DETERMINATION OF THE ELECTRON DENSITY DISTRIBUTIONS IN THE MOLECULES OF HYDROGEN FLUORIDE, WATER AND AMMONIA BY APPLICATION OF THE HELLMANN-FEYNMAN THEOREM.

I. INTRODUCTION

The manner in which the electron density is disposed in a molecule has not received the attention that its importance would seem to merit. In the case of the hydride molecules of ammonia, water and hydrogen fluoride, the two descriptions of their electron distributions currently in vogue are primarily qualitative in nature. Although several S.C.F. calculations for these molecules have been published, the emphasis has been on the predicted energies and dipole moments. Little attempt has been made to correlate the characteristics of the predicted densities with the chemical concepts of hybridization, polarity or ionic character, bond 'bending' and delocalization. The aim of the present work is to determine the electron density distributions in the three molecules by the requirement that the forces exerted by the electron density on the nuclei be equal and opposite to the nuclear forces of repulsion. Proposed distributions, either qualitative or quantitative in origin, can readily be tested by a calculation of the predicted forces. In order to relate the forces satisfactorily to the above properties of the density, the equivalent orbital representation of the wave function is employed. The advantages of using a property of the

one-electron density (such as forces) rather than a function of the two-electron density (such as energies) to examine the three dimensional density will be illustrated by a brief review of the basis and development of the two opposing theories now held about the electronic structure of hydride molecules with lone pairs of electrons.

One of these theories, that which advocates methane-like density distributions through the whole series of molecules considered here, grew out of the detailed investigation by Lennard-Jones and co-workers into the relationship between delocalized molecular orbitals and localized equivalent orbitals (33, 34, 35, 36). Their work elegantly demonstrated that the two modes of description, the first so fruitful in spectroscopy and the second in considerations of bond phenomena, are in reality two sides of the same coin. In a molecule with N electrons, each described by a spin orbital $\varphi_i(X_i)$ defining its spin and spatial co-ordinates, a single determinantal wave function for the system can be set up which satisfies the requirements of the Pauli exclusion principle:

$$\Psi = \frac{1}{(N!)^{1/2}} \cdot \begin{vmatrix} \varphi_1(X_1) & \varphi_2(X_1) & \cdots & \varphi_N(X_1) \\ \varphi_1(X_2) & \varphi_2(X_2) & \cdots & \varphi_N(X_2) \\ \cdots & \cdots & \cdots & \cdots \\ \varphi_1(X_N) & \varphi_2(X_N) & \cdots & \varphi_N(X_N) \end{vmatrix}$$

This total electronic wave function is unchanged when the nuclear framework is subject to any of its symmetry operators since this is equivalent to multiplying the elements of the determinant by numerical factors or to taking linear combinations. Under a unitary transformation of the elements this numerical factor is unity. The molecular orbital and equivalent orbital approaches are two ways of setting up the wave function Ψ. In the first case the orbitals belong to the various irreducible representations of the nuclear symmetry group, while in equivalent orbitals any member of the set may be transformed into any other by the operation of a certain subgroup (such as rotation) of the symmetry group of the molecule (36). Any number of equivalent orbitals can be obtained from a set of molecular orbitals; to take the example of ammonia, three equivalent bond orbitals may be formed by the combination of the two degenerate E type molecular orbitals with either one of the two occupied A type molecular orbitals, or with a linear combination of them. However, in order to satisfy the definition (36) of a lone pair of electrons as a pair of electrons with opposite spins in an orbital localized on one nucleus, the linear combination is chosen so as to make only one orbital bonding with the hydrogens and the other localized on the nitrogen atom. The coefficients of the subsequent unitary transformation can be determined by group theoretic arguments (33,34).

The spatial distribution of electrons as given by these equivalent orbitals is usually discussed within the framework of the two-electron or second order density. Löwdin (37) has pointed out two important factors influencing this distribution. The one effect arises from the operation of the Pauli exclusion principle by the requirement of antisymmetrization of the wave function. If X_i is a function of the space and spin co-ordinates of electron i, the one-electron density can be written as the first order matrix

$$\gamma(X_1'|X_1) = N\int \Psi^*(X_1' X_2 \ldots X_N)\, \Psi(X_1 X_2 \ldots X_N)\, dx_2\, dx_3 \ldots dx_N.$$

The second order matrix is

$$\Gamma(X_1' X_2'|X_1 X_2)$$
$$= \binom{N}{2}\int \Psi^*(X_1' X_2' X_3 \ldots X_N)\, \Psi(X_1 X_2 X_3 \ldots X_N)\, dx_3\, dx_4 \ldots dx_N.$$

The diagonal elements of the density matrices have a simple physical interpretation. $\gamma(X_1|X_1)dv_1$ is the probability of finding one electron with spin and space function X_1 within the volume dv_1 when all the other electrons have arbitrary positions and spins. $\Gamma(X_1 X_2|X_1 X_2)dv_1 dv_2$ is the probability of finding one electron in dv_1 and another in dv_2, irrespective of the other electrons. They are normalized so that

$$\int \gamma(X_1 | X_1) dx_1 = N \quad \text{and}$$

$$\int \Gamma(X_1\ X_2 \,|\, X_1\ X_2) dx_1 dx_2 = \binom{N}{2}.$$

The effect of antisymmetrization is to make each set of indices in the second order density antisymmetric, although the first order density is not affected. As a result it can be shown (37) that $\Gamma(X_1\ X_2 \,|\, X_1\ X_2) = 0$ for $X_1 = X_2$. In other words, the probability density for two electrons with the same spin and space components vanishes. Löwdin terms this a 'Fermi' hole, keeping electrons with the same spin apart. The other effect influencing the spatial correlation in the two-electron density is the mutual repulsion of the electrons, represented by the term e^2/r_{ij} in the Hamiltonian. When $r_{ij} = 0$ this repulsive energy becomes infinitely large and the probability $\Gamma(X_1\ X_2 \,|\, X_1\ X_2)$ becomes very small when the two electrons have the same spatial distribution, irrespective of their spin orientations. Löwdin describes this as a 'Coulomb' hole which surrounds each electron with respect to all other electrons. This 'hole' disappears in the one-electron density, since the probability distribution is considered for a single electron at a time, independent of all the others. The two density matrices are related,

however, by the expression

$$\gamma(X_1'|X_1) = \frac{2}{N-1} \int \Gamma(X_1' X_2 | X_1 X_2) dx_2.$$

Thus while both types of electron correlation are important in determining the energy and the six dimensional density, their effects on the three dimensional density are not immediately apparent.

Lennard-Jones (38) has investigated the spatial correlation of electrons by calculating the probability of finding two electrons in a prescribed configuration in ordinary space. His method applies to electrons of the same spin orientation, since only the 'Fermi' holes arising from the exclusion principle are considered. He finds that the configuration of highest probability in a four electron system is that where four electrons are situated at the corners of a tetrahedron when equivalent orbitals are used to describe the one-electron orbitals. Zimmerman and Van Rysselberghe (39) came to the same conclusion from a calculation of the relative positions of all of the valence electrons in the configuration $(1s)^2(2s)^2(2p_x)(2p_y)$ of the carbon atom. According to Lennard-Jones (38), these calculations show that in the multidimensional space used to describe the co-ordinates of all the electrons there is a point at which Ψ has its maximum value. The position of

the maximum corresponds to that configuration of the electrons for which the vectors joining the electrons to the nucleus in ordinary space are inclined to each other in a particular way. This is said to give rise to a spatial correlation of electrons in an atom, due to the operation of the Pauli exclusion principle.

These results have found a natural application in problems of molecular structure since they provide support (39) for Pauling's theory of directed valence. Gillespie and Nyholm (40) and Pople (30) have discussed the structure of neon and isoelectronic molecules using the results of Lennard-Jones. In the neon atom there are four valence shell electrons of either spin direction, which can be described as occupying two tetrahedra that have mutually independent orientations within the customary orbital approximation which ignores 'Coulomb' correlation. Gillespie and Nyholm consider that when hydrogen nuclei are present this causes the tetrahedra to come into alignment with each other so there are four pairs of electrons arranged tetrahedrally in the methane, water and ammonia molecules. Pople has explained the formation of directed bonds in these molecules in terms of a withdrawal of successive positive charges from the neon nucleus. In hydrogen fluoride the three remaining lone pair orbitals are considered to be much the same as the tetrahedral

orbitals of the neon configuration (he assumes the two spin tetrahedra to coincide in the neon atom). In the water molecule the second proton will be drawn out along a line of maximum density and therefore at roughly the tetrahedral angle to the first proton. The two remaining lone pair orbitals will have strong directional character above and below the plane of the water molecule. To form ammonia, another proton is drawn out along the line of maximum lone pair concentration to yield three bonds and one lone pair in a tetrahedral configuration. Finally in methane a fourth proton is considered to move out along the line of the lone pair direction to form the fourth equivalent bond orbital.

The fact that the observed bond angle in ammonia is 107.3° and in water is 104.45° rather than the predicted $109^{\circ}28'$ is attributed to the fact that electrostatic repulsions between electron pairs in a valency shell decrease in the order

lone pair- lone pair > lone pair- bond pair > bond pair- bond pair (40).

The basis of this order is that the lone pairs are on the average, closer to the nucleus than are the bond electrons and therefore have a relatively large mutual repulsive energy. By combining this theory with electronegativity effects (for instance, replacing a proton by a more

electronegative element is said to move density away from the central atom, thereby decreasing repulsive effects and allowing the bonds to approach more closely) Gillespie and Nyholm (40) succeed in correlating a considerable amount of structural chemistry. Dickens and Linnett (41) have attributed spatial and other effects in the present series of molecules and in various inorganic and organic molecules to electron correlation. Thus they consider that "both spin and charge correlations would cause the angle subtended by the bonding electrons to be less than that subtended by the lone pairs".

A measure of quantitative justification for this description of the electron density in hydride molecules with lone pairs was thought to be provided by the results of calculations by Pople (42) and by Duncan and Pople (43). They examined the molecules of water, ammonia and hydrogen fluoride in terms of localized equivalent orbitals expressed as parameters which related the coefficients to the hybridization and polarity of the electron distribution.[1] The requirements that the orbitals be mutually orthogonal and predict the correct dipole moment sufficed to fix the parameters in water and in ammonia, but one variable remained in hydrogen fluoride. As Pople (42) noted, however, two limitations were made on the form of the equivalent

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[1] The succinct characterization of the density by a few chemical parameters, in the manner first proposed by these authors, will be used extensively in the present work. Such a description immediately clarifies the nature of any predicted distribution.

orbitals for the polyatomic molecules in order to completely define the density. One was that delocalization of the hydrogen atoms was unimportant (i.e. $H_{(i)}$ was assumed to contribute to the bond orbital ψ_i but not to ψ_j) and the second was that the bond orbitals were directed along the bond axes. With these assumptions, the conclusion was reached that the lone pair electrons were in strongly hybridized orbitals. They made the over-riding contribution to the dipole moment, so much so that a predicted bond polarity of $H(\delta-) - X(\delta+)$ was necessary in order to provide a bond moment opposing the excessive lone pair moment. This work reinforced the theory of prominent lone pair electrons in tetrahedrally directed orbitals which had been arrived at by considerations of correlation effects.

The second explanation tendered of the electron distribution in this series of hydride molecules is the older one. Prior to the work of Lennard-Jones and co-workers on equivalent orbitals, the bonds in simple hydride molecules were described as p orbitals overlapping with hydrogen orbitals. The energy difference of $\sim$ 200 k.cals/mole between the 2s and 2p electrons was thought to be too great to permit much hybridization to occur on bond formation. In the simple valence bond theory, the p orbitals of the central atom in a polyatomic molecule are required to be

orthogonal to each other. The predicted bond angle is therefore 90°. While second row and heavier polyatomic hydrides do satisfy this requirement to within a few degrees, there is a very large discrepancy in the first row hydrides of water and ammonia.

Pauling attributes this to the repulsion between the protons, which will have a large effective positive charge when bonded to the strongly electronegative first row elements. However, his calculations indicate that this repulsion can only open the angles by 3° or 4° (44). Coulson (45) mentions another factor that could tend to open the bond angle; the full valence bond treatment considers all possible pairing schemes which would introduce further ionic interactions between the bonds. The final discrepancy can only be removed, however, by the introduction of hybridization in the bond orbital (45). Pauling points out that the tendency to form strong bonds by hybridization is resisted when atoms have lone pair electrons which are more stable in the s orbital. From a very simple variation calculation in which the two opposing tendencies were considered, Pauling predicted 5 % and 6% s character in the bond orbitals of water and of ammonia(44).

If the s electrons in the hydride molecules are not hybridized the description of a tetrahedral distribution

of electrons in the neon atom can be replaced by an $(s)^2(p)^6$ description. Unsöld has shown that completed subshells such as $(p)^6$ have spherically symmetric distributions. The validity of regarding such distributions as directed in space would seem to be questionable. Cuthbert and Linnet (47) have suggested that the stability of the cubic close packed arrangement of atoms in crystals of neon, argon, krypton and xenon (as opposed to the hexagonal close packing in helium) is due to the presence of four unshared pairs of electrons in the valence shell. As Pauling (44) mentions, however, the inherent cubic polarizability of the outer shell in the rare gases would favour cubic close packing in the solid state.

The two theories of the electronic structure of the hydride molecules with lone pair electrons predict very different density distributions. The tetrahedral description appears to possess fewer inconsistencies for hydrides of the first row of the periodic table, and is backed up by the work of Pople and Duncan; but the p bond description is better able to explain the bond angles of heavier hydrides. In the following sections both of these possibilities will be investigated in terms of forces.

Interpretation is simplified by the fact that no correlation effects enter into the description. There is a real, three dimensional density of electronic charge, made up of independent contributions from orthonormal, equivalent orbitals. The equilibrium configuration of any molecule is that in which the attractive electronic force on each nucleus just balances the nuclear repulsive forces. The two parameters that Duncan and Pople discarded turn out to be of crucial importance in the description of this equilibrium configuration. In fact, it will be demonstrated that the apparent stalemate reached by the two descriptions of the density outlined above is due to a correlation of hybridization with molecular geometry. From the energy approach it is not at all obvious why bond bending and delocalization should be important. The stress on correlation energies has no doubt contributed to a feeling that these changes, which concentrate electron density in one region between all the nuclei, would be unfavourable energetically. On the contrary, it will be demonstrated that the most accurate S.C.F. descriptions of the density emphasize this concentration of charge in the binding region of a molecule. It is essential for a good estimate of either a force or an energy. The conclusion can be drawn that the effects of correlation interactions are outweighed by the interactions of the electrons with the

positively charged nuclei. The most probable position of an electron is one where it can be attracted most favourably by the nuclei, rather than one where it is least repelled by the other electrons.

II. THE HYDROGEN FLUORIDE MOLECULE.

Determination of the density distribution.

In order to retain the concept of lone pair electrons the equivalent orbital representation of the hydrogen fluoride wave function is used. Duncan (48) has given the relationship between these orbitals and the symmetry orbitals for hydrogen fluoride. The notation used to describe the orbital parameters is that of Duncan and Pople(43). However, for convenience in discussing and calculating the forces, the three equivalent lone pair orbitals are replaced by one along the bond axis and two $2p_{\pi}$ orbitals perpendicular to the axis. As the sigma lone pair orbital varies from p to s the corresponding equivalent orbitals change from p orbitals directed at right angles to each other, to sp^2 orbitals in a plane through the fluorine atom. In this latter configuration they contribute neither to the force on the fluorine nucleus, nor to the dipole moment. It must be borne in mind that it is not a limiting configuration; by mixing positive p into the sigma lone pair orbital, the equivalent orbitals can be made to point towards the hydrogen atom.

The basis set is composed of Slater atomic orbitals with the orbital exponents obtained by Ransil (4) in a

variation treatment of hydrogen fluoride in which the exponents were optimized. By using these values (termed the B.L.M.O. set in Table III) a meaningful comparison of the S.C.F. and the present results can be made. Two of the fluorine electrons are initially assumed to be localized in the 1s orbital on that atom. In order to retain orthogonality with this inner orbital, both the 2s fluorine orbital and the hydrogen 1s orbital are made orthogonal to the fluorine 1s orbital. They are designated by s and h_o[1]. respectively. The symbol p refers to a 2p orbital directed along the bond axis from fluorine to hydrogen. The orbitals are

$$\psi_o = 1s$$
$$\psi_b = \lambda[\cos\varepsilon_b\ s + \sin\varepsilon_b\ p] + \mu h_o$$
$$\psi_l = \cos\varepsilon_l\ s - \sin\varepsilon_l\ p$$
$$\psi_\pi = p_\pi$$

The three parameters appearing in these expressions are the same as those described in Part I. The bond polarity is λ/μ, the bond hybridization is ε_b and the lone pair hybridization is ε_l. The absolute values of λ and of μ are determined by normalization of the bond orbital. In the

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[1]. This orbital does not contain the normalizing factor.

treatment of Duncan and Pople[1] (43) the parameter ε_b was fixed by the orthogonality requirement between ψ_b and ψ_1 and λ/μ was chosen to fit the correct dipole moment. There still remained one degree of freedom, ε_1, which allowed the equivalent lone pair orbitals to vary from p to sp^2 in character.[2] In the present case this last parameter is fixed by the requirement that the force exerted on the proton by the density distribution be equal and opposite to the nuclear force of repulsion. Figure 8 illustrates how the force on the hydrogen nucleus changes with ε_1 for densities satisfying the dipole moment criterion.[3] It is evident that the lone pair has to become pure s before the electronic force balances the nuclear force of nine atomic units. In order to meet the small residual force at $\varepsilon_1=0$ (0.06a.u.) it is necessary to let ε_1 go negative and hence have the equivalent orbitals pointing towards the hydrogen nucleus.

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1. In their approach they assumed that the non-orthogonality between the 1s and hydrogen orbitals (0.049) was small enough to be ignored. Inclusion of this amount of 1s in the bond orbital really does have a negligible effect on the parameters, the dipole moment and the force on the proton, but it is important for the force on fluorine because of the magnitude of the 1s-p atomic force term.

2. The inability of these orbitals to attain the sp^2 form, as noted by Duncan and Pople, was due to their restriction that the coefficient of 2s in the bond orbital remain positive. Orthogonality requirements for this situation give rise to a small amount of negative 2s in the bond orbital.

3. In the figures and discussion referring to hydrogen fluoride the forces are given in units of $1/R^2$, where R is the bond length. Thus to obtain the absolute force in atomic units the numbers must be divided by 3.00329. Explicit expressions for the forces are given in the Appendix.

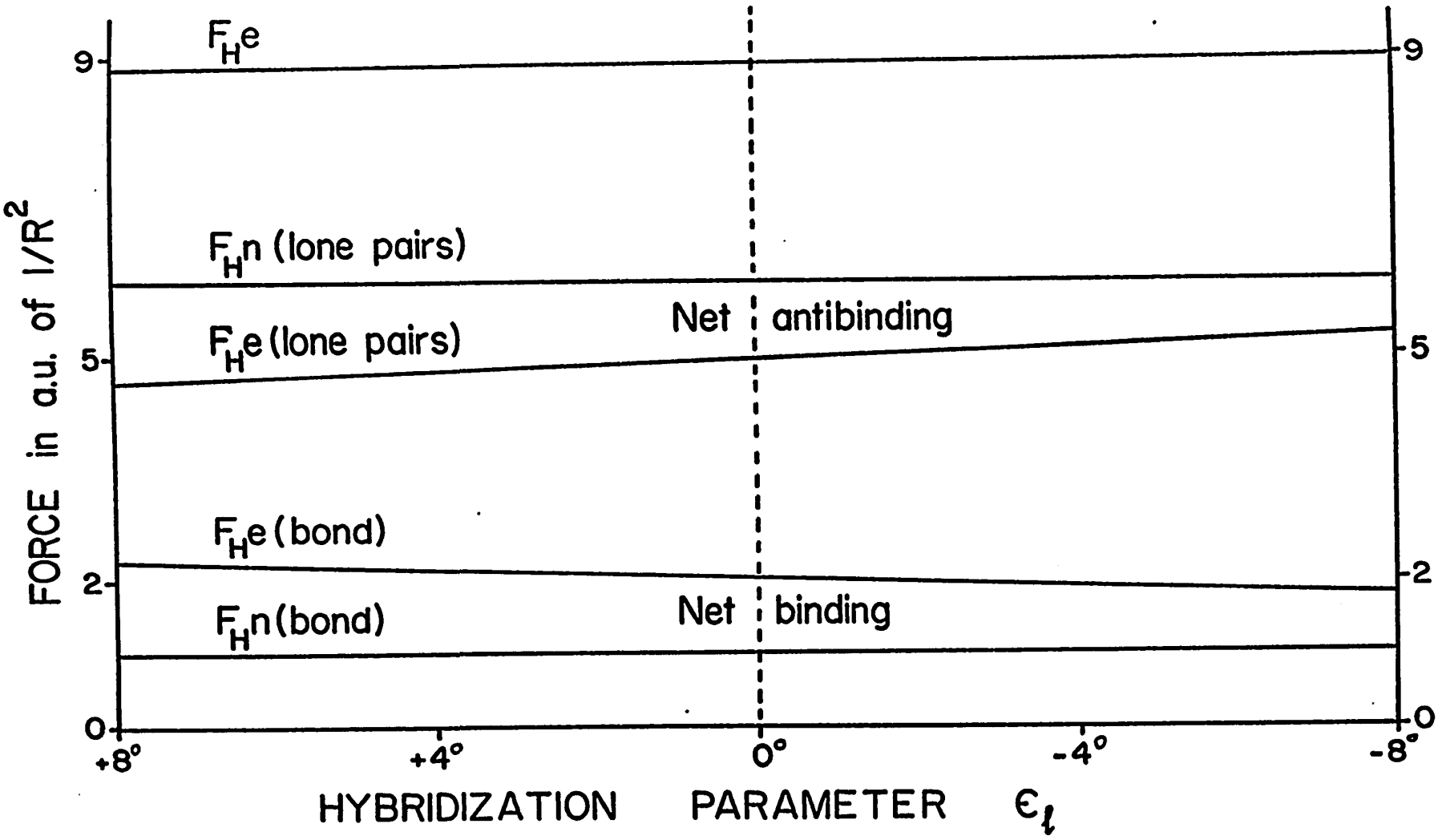

FIGURE 8. The forces exerted on the proton in HF by the lone pair and bond orbital electron densities as a function of the lone pair hybridization parameter ϵ_1. $F_H n$ refers to the force due to the number of nuclear charges associated with the six lone pair electrons or the two bond electrons in the separate atoms. The orbitals are net binding if $F_H e > F_H n$ and net antibinding if $F_H e < F_H n$. (All forces in units of $1/R^2$).

The reason for this surprising prediction of negative ε_1 can be found in the orbital contributions to the force on hydrogen. The inner shell electrons on fluorine always shield two units of positive charge and form a non-binding orbital. The four electrons in p_π orbitals shield only three units of nuclear charge as opposed to four in the neutral atom and are therefore net antibinding. The shielding due to the third lone pair orbital increases as ε_1 decreases (the p_π contribution is of course independent of ε_1), since density piled up behind the fluorine nucleus is ineffective at shielding it from the proton. In order to achieve complete shielding, this orbital actually has to concentrate density between the nuclei. The bond orbital provides all of the binding force. The absolute magnitude of this binding force decreases as ε_1 tends to zero, on account of the necessary increase in the amount of negative s in the bond orbital. In spite of this adverse hybridization, the bond orbital provides sufficient electronic force to balance the nuclear repulsion when the sigma lone pair orbital does its share in screening the nucleus.

On examining the force on the fluorine nucleus, as shown in Figure 9, it is obvious that if this nucleus is to be anywhere near electrostatic equilibrium there is no possibility of lone pair hybridization in the conventional direction. The electronic force is actually in the same

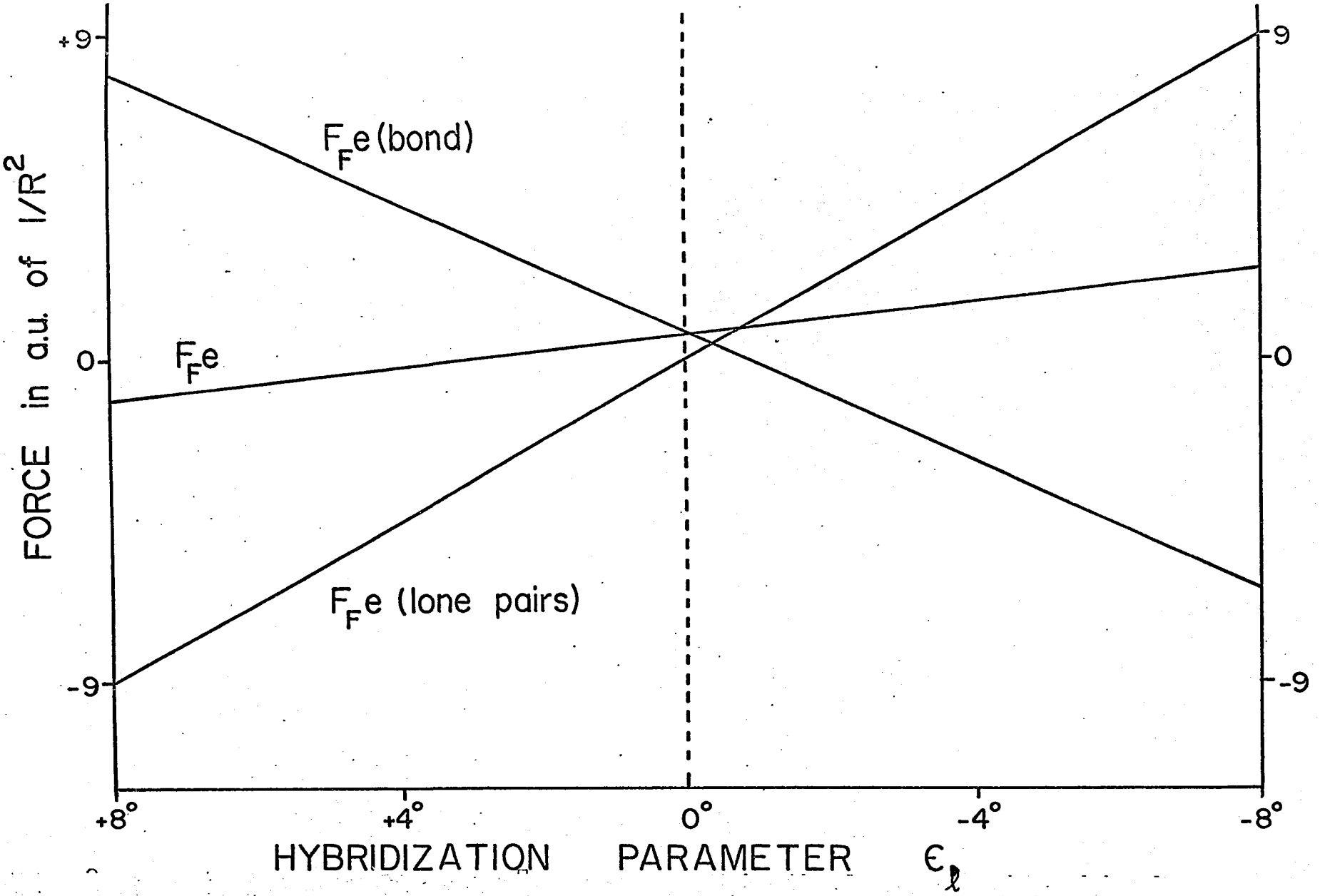

FIGURE 9. The forces exerted on the fluorine nucleus in HF by the lone pair and bond orbital electron densities as a function of the lone pair hybridization parameter ϵ_l. F_Fe is the total electronic force. (All forces in units of $1/R^2$).

direction as the nuclear force of repulsion when ε_1 is positive and becomes zero around $\varepsilon_1=0$. (If the h orbital is not made orthogonal to the 1s orbital the electronic force increases to two-thirds of the nuclear repulsion at this point.) It is obvious that the orbitals chosen are not flexible enough to provide a good description of the density around the fluorine nucleus. In order to balance the force on fluorine with this set of orbitals it would be necessary to invoke large negative values of ε_1, inconsistent with the results for the force on the proton. One additional parameter can be introduced, to be fixed by the requirement that the net force on the fluorine nucleus be zero.

Inner shell polarization.[1]

The major defect in the molecular orbitals lies in the limitation of the inner shell orbital to 1s character. All complete variation calculations predict small amounts of 2s and 2p in this orbital. Since the force on fluorine is very sensitive to such p character this coefficient is chosen as the final parameter to be varied. Introduction of p into ψ_o makes this orbital non-orthogonal with ψ_b and with ψ_1. Rather than alter the lone pair description, 2s is

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1. As Mulliken (49) has pointed out, the dividing line between mixing which should be termed hybridization as opposed to polarization is ill-defined. Here hybridization will be limited to the mixing of 2s and 2p in valence orbitals which are occupied in the free atom.

included in the inner orbital to satisfy the orthogonality requirement with the lone pair orbital. In the bond orbital, the coefficient of 1s is fixed by the orthogonality requirement with the entire inner shell orbital rather than by 2s-1s orthogonality. To meet this end the s orbital in ψ_b is replaced by $s_q = N_q (s' - q\ 1s)$ where $s = N_o (s' - S\ 1s)$. Here S is the overlap between the nodeless 2s orbital, denoted by s', and 1s; q is the parameter to be determined by the orthogonality requirement, and N_q and N_o are the normalizing factors.[1] The new inner shell orbital is written as

$$\psi_o = c_1\ 1s + c_2\ s' + c_3\ p.$$

Two normalizations have to be performed. For ψ_o the condition is

$$c_1^2 + c_2^2 + c_3^2 = 1$$

and for ψ_b the condition can be used to calculate λ and μ once λ/μ is known,

$$\mu^2 = 1/[1 - S_1^2 + (\lambda/\mu)^2 + 2(\lambda/\mu)(\cos\varepsilon_b N_q(S_2' - S\ S_1) + \sin\varepsilon_b\ S_3)]$$

The overlaps between the h orbital and the 1s, s, s' and p

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1. This change means that the parameter λ has been defined slightly differently. However, a comparison of the values of λ/μ found from this orbital and from that written as $\cos\varepsilon_b\ s + c\ 1s$ shows that the difference is insignificant.

orbitals are denoted by S_1, S_2, S_2' and S_3 respectively. Three orthogonality conditions have to be satisfied;

(i) $\int \psi_b \psi_1 d\tau = 0$ (ii) $\int \psi_o \psi_b d\tau = 0$ (iii) $\int \psi_o \psi_1 d\tau = 0$,

and these give rise to the following equations relating the bond parameters.

(i) $$\frac{N_q}{N_o} = \frac{-S_2 + \tan\varepsilon_1 (S_3 + \lambda/\mu \sin\varepsilon_b)}{\lambda/\mu \cos\varepsilon_b}$$

(ii) $$\lambda[\cos\varepsilon_b N_q (c_1 S - q c_2 S + c_2 - q c_1) + \sin\varepsilon_b c_3]$$

$$= \mu[c_2 S_1 S - c_2 S_2' - c_3 S_3]$$

(iii) $$c_2 = c_3 \tan\varepsilon_1$$

The last two equations can be combined to yield an expression for c_3,

(iv) $$c_3 = \frac{\lambda/\mu \cos\varepsilon_b N_q (q - S)}{S_3 + \lambda/\mu \sin\varepsilon_b + \tan\varepsilon_1 [S_2 + \lambda/\mu \cos\varepsilon_b N_q N_o (1 - q S)]}$$

The orthogonality requirement between the equivalent lone pair orbitals, which does not arise in the present description of the orbitals, serves to relate the angle β between these orbitals to the equivalent orbital hybridization parameter ε_1'.

(v) $\cos\beta = -\cot^2\varepsilon_1'$ where $\cos\varepsilon_1' = (1/\sqrt{3})\cos\varepsilon_1$.

These conditions also apply to the basis set without inner shell polarization, in the special case when q = S. Then both c_2 and c_3 are zero and equation (i) can be used to evaluate ε_b. This limiting value of $\cos\varepsilon_b$ is found from the rearranged equation (i),

(vi) $\cos\varepsilon_b = \cos^2\varepsilon_1 \left(c + \tan\varepsilon_1\sqrt{1 + \tan^2\varepsilon_1 - c^2}\right)$

where $c = [S_3 \tan\varepsilon_1 - S_2]/(\lambda/\mu)$

Equation (vi) is used to evaluate ε_b for different ranges of ε_1 and of λ/μ in this limiting case.

In order to obtain a positive coefficient of p in ψ_o it is necessary to decrease q. This reduces the ls-p atomic force contribution to the bond orbital (since $\cos\varepsilon_b$ is negative) and consequently, the binding power of this orbital for the fluorine nucleus. However, the atomic force generated by the inner shell polarization outweighs this loss. The alternative polarization, where q is increased and the coefficient of p is negative, is very unfavourable in terms of forces and can be discarded. Machine computation was employed to evaluate the parameters, forces and the dipole moment. Basically ε_1 was chosen to give a good force on the hydrogen nucleus, then c_3 was increased to balance the force on the fluorine nucleus. The dipole moment was fixed by an appropriate choice of the polarity, λ/μ. Further details are presented in the Appendix.

TABLE I.

Parameters for densities predicting electrostatic equilibrium in HF.

ε_1	λ/μ	ε_b	c_3	c_2	$F_H e$ (in $\frac{1}{R^2}$ a.u.)	$F_F e$ (in $\frac{1}{R^2}$ a.u.)
3°	1.5786	104° 8'	0.0893	0.0048	8.922	9.000
0°	1.6150	106° 48'	0.0829	0.0000	8.945	9.000
-6°	1.6845	112° 46'	0.0696	-0.0075	8.989	9.000

The results are given in Table I. It is found that with this extra flexibility it is possible to attain electrostatic equilibrium, at a negative value of ε_1. The force on hydrogen has barely changed at a particular ε_1 from the value it had when there was no inner shell polarization, while the force on the fluorine nucleus has increased from about zero to nine atomic units. Small shifts in charge density close to the heavy nucleus do not alter the penetration force exerted on the proton. Each density listed has a dipole moment equal to the experimental value of 1.82 Debyes. The predicted bond polarity is high, of the same order as that calculated by Coulson (50) for a very simple model of a p orbital on fluorine overlapping with a hydrogen orbital. This qualitative approach, in which the overlap contribution to the dipole moment is ignored, yields a polarity of 1.80

to account for a dipole moment of 1.82 Debyes. The amount of negative s character in the bond orbital of the electrostatic density is 15% at $\varepsilon_1 = -6^\circ$.

The coefficient of p introduced into ψ_o to balance the force on the fluorine nucleus is 0.07, which is much larger than the coefficient of p that appears in a variational calculation. Much more effective polarization can be obtained using a 'shrunken' p orbital which is dense in the same regions of space as the inner orbital. By far the most powerful polarizing orbital for the 1s density is a '1p' orbital, given by $\cos\theta \exp.(-\zeta r)$. This is the form taken by a 1s orbital when perturbed by a small nuclear displacement. For the same exponent as the 1s orbital, a coefficient of 0.008 is sufficient to meet a force of nine a.u. on the fluorine nucleus. Since the overlap between such an orbital and the valence orbitals is very small, the valence contributions to the force remain the same as in Figure 9, but an additional positive force is added at each ε_1 to make the force on the fluorine nucleus equal to nine a.u. This would imply that the valence electrons contribute nothing to the field at this nucleus; the inner shell orbital experiences the field due to the proton and polarizes to give a field equal in magnitude and opposite in direction. Inner shell polarization has been studied by Sternheimer (51). He pointed out that a

spherical distribution of charge, when in the presence of an external electric field, will polarize to the extent necessary to overcome the force exerted by this field. Unfortunately, no variation calculation has been performed for hydrogen fluoride where special allowance is made for inner shell polarization by the introduction of additional orbitals of the type discussed above.[1] On the other hand, valence shell polarization has been investigated very thoroughly for hydrogen fluoride in the detailed treatments of Nesbet (52) and of Clementi (53). It is necessary to examine this mode of polarization as an alternative to inner shell polarization.

3d valence shell polarization.

Introducing a 3d polarizing orbital of the same effective radius as the 2p orbitals (the best free atom value of 2.55 is chosen for the orbital exponent) concentrates density between the nuclei. As shown schematically in Figure 10, p_σ-d_σ polarization has more effect on the forces along the bond than has the corresponding π polarization. In π overlaps the density is concentrated around the internuclear axis, rather than along it, which reduces the forces exerted by a factor of two-thirds. Compensating

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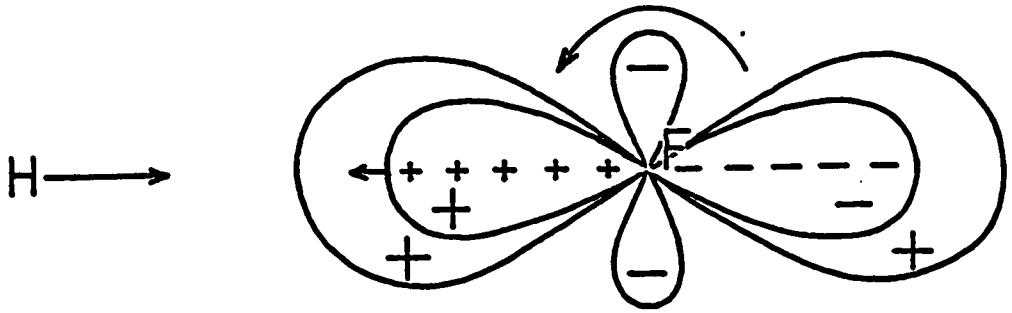
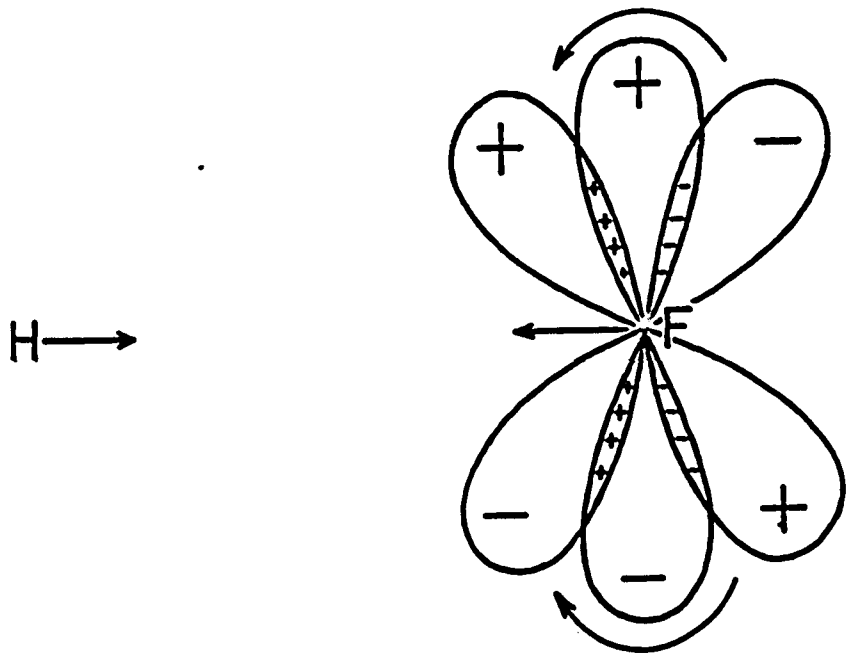
1. It will be shown that the predicted force on the fluorine nucleus for variation calculations employing a limited basis set is simply equal to the nuclear force of repulsion.



a). $3d_\sigma - 2p_\sigma$ POLARIZATION



b). $3d_\pi - 2p_\pi$ POLARIZATION

FIGURE 10. A schematic representation of the forces arising in HF from the density shifts due to $2p_\sigma$-$3d_\sigma$ and to $2p_\pi$-$3d_\pi$ polarization.

for this in hydrogen fluoride is the fact that there are twice as many electrons able to undergo d_π as compared to d_σ polarization. Therefore both types of polarization must be investigated.

The parameter c_3 introduced previously is replaced by $c_4 d_\sigma$ in the bond orbital or $c_5 d_\pi$ in the π orbitals. The ψ_b-ψ_1 orthogonality condition is not altered by the inclusion of 3d, but the presence of $3d_\sigma$ necessitates a renormalization of the bond orbital. This new condition can be written

$$\mu = -c_4 S_4/a + [(1-c_4^2)/a + c_4^2 S_4^2/a^2]^{\frac{1}{2}} \quad \text{where}$$

$$a = 1 - S_1^2 + (\lambda/\mu)^2 + 2(\lambda/\mu)[\cos\varepsilon_b\, S_2 + \sin\varepsilon_b\, S_3]$$

and S_4 is the overlap between the h and d_σ orbitals. Using these orbitals it is possible to investigate how much 3d participation is required to balance the force on the fluorine nucleus. Typical results are listed in Table II, for densities satisfying the dipole moment criterion.

Invoking 3d participation cannot of itself enable the system to attain electrostatic equilibrium. In order to balance the force on the fluorine nucleus, density in the outermost regions of the atom has to concentrate between the nuclei. This density exerts a force on the proton which is larger than the nuclear force of repulsion.

TABLE II.

Parameters and forces for densities with 2p-3d polarization in HF.

ε_1	λ/μ	ε_b	$c_5(d_\pi)$	$c_4(d_\sigma)$	$F_H e(\text{in } \frac{1}{R^2 \text{ a.u.}})$	$F_F e(\text{in } \frac{1}{R^2 \text{ a.u.}})$
0°	2.123	$101^\circ\ 51'$	0.0772	-	9.303	9.000
10°	2.143	$90^\circ\ 4'$	0.0912	-	9.323	9.000
0°	1.660	$105^\circ\ 21'$	0.0100	-	8.986	1.845
0°	2.215	$101^\circ\ 27'$	-	0.1360	9.509	9.000
10°	2.245	$89^\circ\ 37'$	-	0.1726	9.606	9.000
0°	1.640	$105^\circ\ 27'$	-	0.0100	8.985	1.368

To decrease the net force on the proton, while keeping the net force on fluorine equal to zero, one would have to go towards large negative ε_1. Alternatively a 2p orbital pointing away from the fluorine nucleus could be introduced on the hydrogen nucleus, to oppose the force exerted on the proton as a result of 3d polarization. Neither of these solutions are satisfactory. Since the valence hybridization can quite adequately describe the correct force on the proton, it seems unlikely that any second-order polarization effects should result in a large rearrangement of the forces exerted on that nucleus.

The answer obviously does not lie solely in 3d participation. An upper limit to the amount of such participation can be estimated by considering those distributions, with both inner and valence shell polarization, which predict the correct force on the proton.

(i) No 3d participation. From Figure 9 it can be seen that the force on fluorine is 2.5a.u. when the proton reaches equilibrium at $\varepsilon_1 = -8^\circ$. The difference of 6.5a.u. is provided by inner shell polarization.

(ii) The 3d coefficient is about 0.01. Two such points are listed in Table II. That force on the proton which was provided by negative lone pair hybridization in case (i) is replaced by the contribution from 3d polarization. The predicted force on fluorine is slightly decreased e.g. for $c_5 = 0.01$ the force on the proton is correct at $\varepsilon_1 = 0^\circ$, but the force on fluorine has decreased to 1.85a.u.

(iii) More 3d participation. To balance the force on the proton, the lone pair orbitals have to form hybrids behind the fluorine nucleus, with a resultant <u>overall decrease</u> in the force on fluorine.

The force on hydrogen can be balanced with the largest concomitant electronic force on fluorine and the minimum consequent inner shell polarization in case (i).

The coefficient quoted in case (ii) is likely to be an upper limit, because the binding force attributed there to 3d may partly arise from other orbitals not considered. In terms of atomic forces, the 3s and 3p orbitals are much less effective at polarizing the valence shell than are the 3d 'shrunken' orbitals examined here.

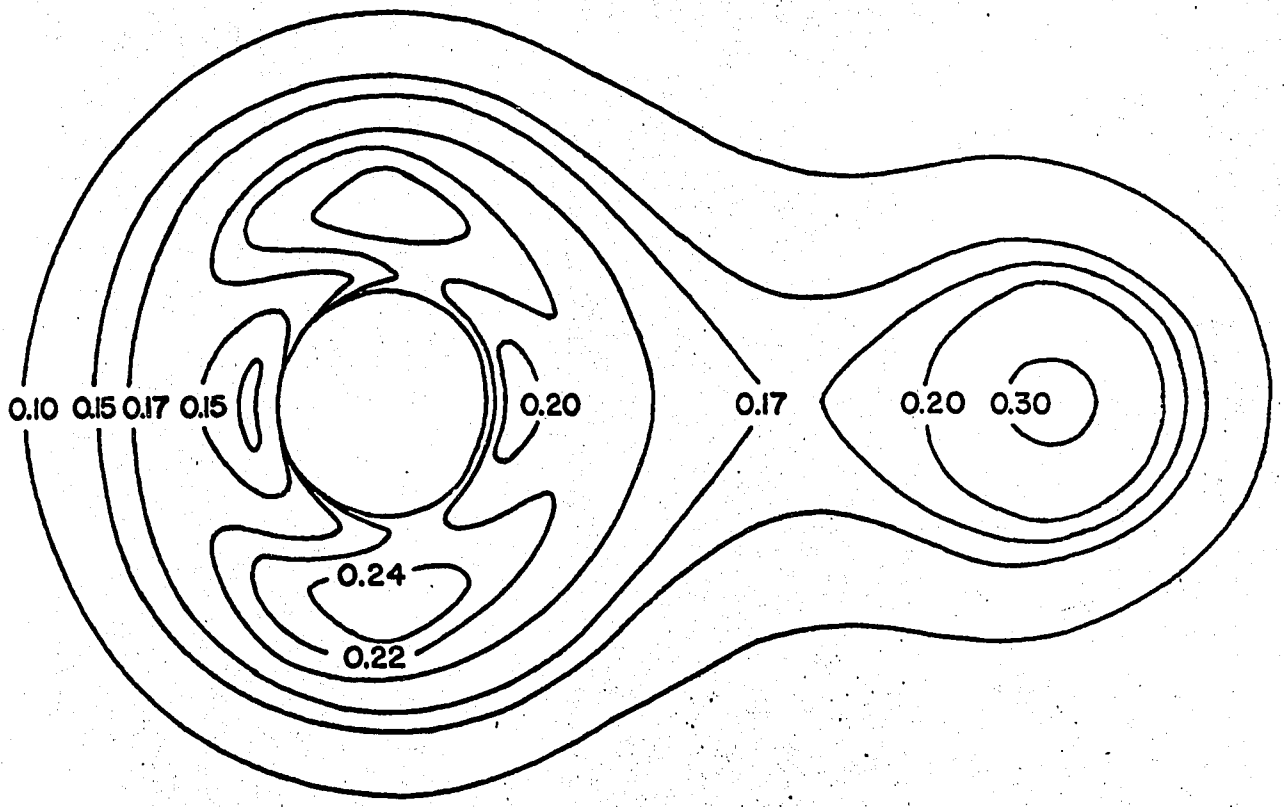
It has to be concluded that inner shell polarization is the most economical method of attaining electrostatic equilibrium, particularly if a suitable orbital is included in the basis set. A minimum amount of deformation on bonding is required: the two 1s electrons on fluorine shield their share of nuclear charge whether or not they polarize to some extent, the 2s electrons remain in their non-binding orbital, and the binding force built up in the bond orbital counteracts the antibinding of the π electrons. Valence shell polarization would serve to help the binding in the σ orbital or to decrease the antibinding in the π orbitals.

Sternheimer has calculated the electric field at various nuclei of atoms and ions when they are subject to an external perturbing field (51). In the alkali atoms he found a large contribution to the field from the valence s electron on perturbation (54) and concluded that this was balanced by the induced inner shell polarization.

However, in his calculations on the fluoride ion (55) he found that the largest contribution to the electric field came from a p-d type perturbation. For this calculation the inner shell was approximated by a Slater 1s orbital, as opposed to analytical Hartree-Fock orbitals for the valence electrons. Sternheimer estimated an error of ± 20 % in the inner shell contribution as a result, but since it was small compared to the contributions from the valence shell electrons, he noted that the final result was hardly affected. It appears, therefore, that the diffuse negative fluoride ion is much more susceptible to valence shell polarization than is the neutral fluorine atom taking part in bond formation.

Density contour map.

A density contour map for the electrostatic density is plotted in Figure 11. Details of the method used to compute the contour lines are given in the Appendix. Only the valence orbitals are shown, the density at the fluorine nucleus arising from the 1s present in the lone pair and bond orbitals by orthogonality. The orbitals contribute to the density mainly in a plane through fluorine perpendicular to the bond axis. This appears in the diagram as relatively dense lobes above and below



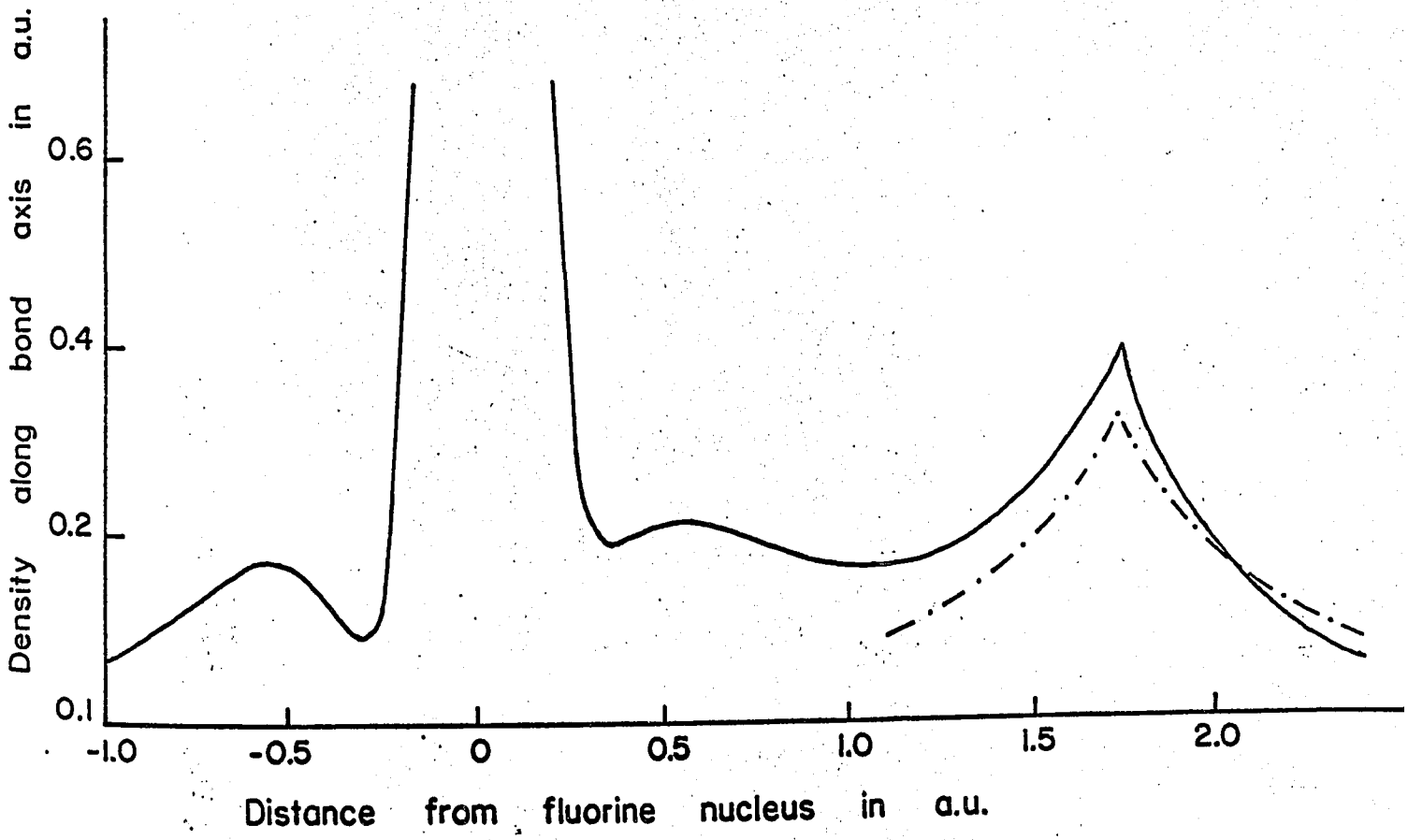


FIGURE 11. A density contour map in a.u. of the valence electrons in a plane through the HF molecule. Below it is shown the density concentration along the bond axis and in an isolated hydrogen atom (dashed line).

the fluorine nucleus. An apparent 'cave' exists behind the fluorine nucleus, since the electron in the p_σ orbital is concentrated between the two nuclei. The formation of a zigzag $(HF)_n$ polymer with an F..F..F angle of about 120° (56) can readily be pictured. The proton of an approaching HF molecule carries a net positive charge due to the large bond polarity. It will be attracted to the most negative region of the fluorine atom, but will simultaneously be repelled by the hydrogen nucleus. The presence of external centres of charge alters the conditions for electrostatic equilibrium and hence the requirement that the sigma lone pair electrons be in a 2s orbital. Therefore the density in Figure 11 and that observed in the associated molecule are in no way incompatible.

The graph plotted below the density contour map shows how the density varies along the internuclear axis. The dotted line represents the density distribution of an isolated hydrogen atom on the same scale. Two factors determine the peak height at the proton in the molecule; the bond polarity removes density from the region of the proton as it increases, and the increased orbital exponent concentrates the density remaining at the proton. The combined effect keeps the density at the proton very close to the value it had in the isolated atom. Behind the proton, the two distributions fall off in much the same manner but,

as might be expected, the concentration along the axis between the nuclei is increased by bond formation. A principle of minimum deformation appears to govern the behaviour of the density around the proton. This distribution remains as close to that of the isolated atom as is feasible with bond formation. It can be understood why poor results are obtained when the orbital exponent of the hydrogen h orbital is taken as unity in hydride molecules. A far closer approximation to 'atoms in molecules' is provided when the orbital exponents are optimized than when they are kept at the free atom values. It is apparent that the charge shift from one nucleus to another is over-emphasized when only the polarity is considered without suitable optimization of the exponents. This is perhaps the reason for the very large transfer of charge found by Daudel and co-workers (57) in lithium hydride.

Densities obtained from S.C.F. calculations.

Ransil (4) has performed variation calculations for hydrogen fluoride using the same limited basis set of orbitals as those employed for the force calculations. He investigated the effect on the energy and dipole moment

of varying the orbital exponents from the Slater free atom values through the 'best atom' values to the 'best molecular orbital' values. In order to see whether the resultant gain in dissociation energy is associated with a large density rearrangement, the 2σ and 3σ symmetry orbitals can be combined to form a lone pair and a bond orbital by using the criterion of localization. These orbitals are then expressed in terms of the bond parameters defined earlier. The results are presented in Table III.

The most noticeable change is in the polarity λ/μ, as reflected in the increasing dipole moment. To meet the observed dipole moment this ratio would have to increase to $\sim$ 1.6. The lone pair orbital is almost s in each case (ε_1 is approximately 5°) and the bonding arises from a p orbital on fluorine with negative s character. In these S.C.F. densities the dipole moment arises almost solely from the density in the bond orbital, due to the small ε_1. This appears to contradict the findings of Nesbet (52) for his density, which is based on flexible Hartree-Fock orbitals and yields a greatly improved dissociation energy of 4.438 e.v. He transformed the 2σ and 3σ symmetry orbitals into a 'lone pair' orbital and a 'bond' orbital using the criterion proposed by Foster and Boys[1] for

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1. The criterion is that of maximizing the product over all pairs of orbitals of the square of the distance between the centroids of the probability distributions described by orbitals (58).

TABLE III.

Orbital exponents and bond parameters for limited L.C.A.O. S.C.F. densities for HF obtained by Ransil (4).

	SAMO[1]	BAMO[2]	BLMO[3]
$\zeta_{1s}(F)$	8.70	8.6501	8.6533
$\zeta_{2s}(F)$	2.60	2.5639	2.5551
$\zeta_{2p_\sigma}(F)$	2.60	2.5489	2.66[illegible]
$\zeta_{2p\pi}(F)$	2.60	2.5489	2.4965
$\zeta_{1s}(H)$	1.00	1.0000	1.3163
Dissociation energy e.v.(6.06e.v.)	1.21	1.34	2.56
Dipole moment in Debyes (1.820 D)	0.878	1.12	1.44
λ/μ	1.194	1.294	1.377
ε_b	106°54'	105°17'	100°23'
ε_1	5°35'	4°43'	6°41'
β	119°32'	119°40'	119°20'

1. SAMO - Slater atom molecular orbitals
2. BAMO - Best atom molecular orbitals
3. BLMO - Best limited molecular orbitals.

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localized exclusive orbitals, and concluded that the major contribution to the dipole moment in hydrogen fluoride was due to the lone pair electrons.

The discrepancy here lies in the two definitions of a lone pair orbital. By the very nature of the transformation performed in the construction of exclusive orbitals, these would be expected to consist of four prominent 'lobes' of density. This would indeed result in a large contribution to the dipole moment from the three orbitals which are directed away from the hydrogen nucleus, but which contain an appreciable negative contribution from the hydrogen orbital (in Table X of Nesbet's paper the three 'lone pair' orbitals contain -0.071545 of hydrogen 1s). The definition employed in the present approach, which makes the lone pair orbital that involving no hydrogen contribution, becomes indeterminate when more than one orbital or exponent is used to describe the density on the hydrogen nucleus. This is the situation in the case of Nesbet. A lone pair orbital can still be constructed from his symmetry orbitals such that it does not contain hydrogen 1s, but it then has a very small amount of negative 2s contribution from hydrogen. Nevertheless, it is found that the general features shown by the orbitals after this transformation are remarkably similar to those exhibited by limited S.C.F. functions and by the electrostatic density. The lone pair orbital is s with a small amount of positive p, and the bond orbital is an h - p bond, containing less negative s than appears in the

functions listed in Table III. Numerical values cannot be ascribed to the various parameters since most of the orbitals are described by more than one orbital exponent. However, each contribution to a particular orbital appears with the same sign and is the same order of magnitude, which permits one to make the above generalizations. It can be seen that under this transformation most of the dipole moment would arise from the bond moment.

The general characteristics of the density in hydrogen fluoride as predicted by energy calculations therefore correspond much more closely to those exhibited by the electrostatic density than to the qualitative picture of a tetrahedrally hybridized fluorine atom. Appreciable lone pair hybridization is unfavourable both in terms of energies and in terms of forces. Both the Hartree Fock density of Nesbet and the electrostatic density predict a small concentration of the lone pair electrons between the two nuclei. The electrostatic density predicts more bond hybridization than any of the energy densities, corresponding to 15% s character. This again is not bond hybridization in the accepted sense, for the coefficient of s is negative in every density.

Electron population analyses of the densities obtained from variational calculations have been used to

examine how the electron distribution alters as the basis set of orbitals is changed (49,50). This type of analysis, first detailed by Mulliken (60), uses the coefficients obtained from a variational calculation as a measure of the electron 'population' in each atomic orbital or in the overlap region. The significance of such numbers, which often vary considerably with choice of basis set, has been questioned (61) but the method is widely applied. Recently Mulliken himself (49) pointed out that the numbers are most useful in a comparison of wave functions for the same molecule; they do not provide an absolute test of a wave function. In the assignment of 'gross' atomic populations the overlap between two orbitals is divided equally between them, so that the sum of the gross atomic populations is equal to the number of electrons in the system. Mulliken (49) found from an investigation of the gross atomic populations for hydrogen fluoride wave functions that the population of the p orbital increases at the expense of that of the h orbital as the energies improve and the dipole moments increase. The 'net ionicity' of the bond therefore increases, in agreement with the increasing polarity factor λ/μ observed in the equivalent orbitals in Table III. The population of the s orbital stays constant for Ransil's three cases, which would be indicated from the equivalent

orbitals where the amount of hybridization remains fairly constant. Hence both approaches yield essentially the same information, but in the equivalent orbital notation the changes in population are expressed as changes in parameters commonly used to describe chemical bonds, e.g. hybridization.

It has been customary to use the overlap populations obtained from such an analysis to classify the bonding character of symmetry orbitals. A positive overlap population indicates a bonding orbital, negative overlap an antibonding orbital and no overlap means the orbital is non-bonding. It is proposed that a more meaningful definition would be based on the forces exerted by the density in the orbitals on the nuclei. Since the magnitude of the force depends on the magnitude of the overlap in an orbital, as well as where this overlap is placed, the correlation between bonding character of an orbital as obtained by the two approaches might be good. But forces have the tremendous advantage that they are physically meaningful - it is known what the total electronic force must be for the true wave function of the system. On the other hand, the total overlap population is a nebulous quantity with no particular significance. Another advantage of the use of forces is that the classification of molecular orbitals would be in no way

dependent on the number or nature of basis orbitals used. As Mulliken (49) mentioned, an electron population analysis runs into difficulties when additional polarizing orbitals are added to the basis set, and becomes meaningless when the electron density is described by a one centre approximation.

Force analysis.

A breakdown of the total electronic force into its components can provide insight into the nature of the interactions leading to bond formation and electrostatic stability. There are two ways of performing such a breakdown: either the total contributions from the three types of force can be examined, irrespective of the orbital from which they arise, or the orbital contributions can be compared with the appropriate nuclear repulsions, as determined by the shielding each orbital would provide in the separated atoms. The first approach is most fruitful for the fluorine atom, where the magnitude of the atomic forces detracts from the significance of orbital contributions. These orbital forces can be radically altered, although the total remains invariant, by changing the order of the orthogonalization procedure. The question that can be examined for such an atom is whether the total charge polarization, as measured

by the atomic forces, can balance the net field arising from the repulsive field of a partially shielded proton and the attractive field of the overlap charge.

The second method lends itself readily to an investigation of the force on the hydrogen nucleus. This atom shows the most marked changes on bond formation, as evidenced by the increase in orbital exponent and the low bond polarity. It is therefore most meaningful to discuss the binding character of the molecular orbitals with respect to the hydrogen nucleus. The detailed contributions to the forces on the proton are given in Table IV, for the S.C.F. density determined by Ransil and for the best electrostatic density with $\varepsilon_1 = -6^o$ and inner shell polarization. The orbital contributions will be considered separately.

Inner shell orbital:

Both distributions predict this orbital to be essentially non-binding. The slight binding force arising in the electrostatic distribution is due to inner shell polarization. This orbital is classified as non-bonding in the system based on overlap populations, in agreement with the present description.

Lone pair orbitals:

In both cases the four π electrons shield only three units

TABLE IV

Force on the hydrogen nucleus in HF in units of $1/R^2$ a.u.

(i) Electrostatic density.

	Overlap force	Penetration force	Electronic force	Nuclear force	F_H
ψ_o	0.000	2.018	2.018	-2.000	0.018
ψ_b	0.696	1.098	1.794	-1.000	0.794
ψ_l	0.000	2.106	2.106	-2.000	0.106
$2\psi_\pi$	0.000	3.071	3.071	-4.000	0.929
Total	0.696	8.293	8.989	-9.000	0.011

(ii) Best limited S.C.F. density.[1]

	Overlap force	Penetration force	Electronic force	Nuclear force	F_H
1σ	-0.001	2.001	2.001	-2.000	0.000
2σ	0.376	1.765	2.141	-2.000	0.141
3σ	0.570	0.965	1.535	-1.000	0.555
ψ_l	0.000	1.632	1.632	-2.000	-0.368
ψ_b	0.946	1.098	2.044	-1.000	1.044
$2\psi_\pi$	0.000	3.071	3.071	-4.000	-0.929
Total	0.945	7.802	8.747	-9.000	-0.253

1. 2σ and 3σ are the symmetry orbitals from which ψ_b and ψ_l are obtained.

of charge are therefore net antibinding. However, the two electrons in the σ lone pair orbital are slightly binding in the electrostatic density and quite strongly antibinding in the S.C.F. density. This is a result of the small concentration of charge between the nuclei in the first case and behind the nucleus in the second case. These lone pair electrons obviously play a very different role to the 1s electrons, a difference brought out in the forces but not in the overlap populations.

Bond orbital:

The S.C.F. density predicts a greater net binding force from this orbital than does the electrostatic density. Nevertheless, the latter has a net force on the proton almost equal to zero, compared to -0.253a.u. for the S.C.F. density. The reason for this discrepancy in the S.C.F. force lies in the poor shielding provided by its sigma lone pair orbital, for which $\varepsilon_1 = 6^{\circ}\ 41'$. A low polarity also contributes to increase the net force for Ransil's wave function.

Symmetry orbitals:

Mulliken's correlation of bonding power with overlap population relates the numerical value of the coefficients of the overlap forces to the bonding power. If the overlap forces were similar in magnitude this would

establish a proportionality of the type assumed by Mulliken. As previously pointed out, however, a p_σ orbital overlapping with a hydrogen orbital results in a much greater force than an s - h overlap, although the latter is numerically larger. Since the fluorine contribution to the 2σ orbital is primarily s, the overlap population is 0.265 for this orbital compared to 0.117 for the 3σ orbital, which contains more p. Consequently the overlap population criterion rates the 2σ as the most strongly bonding orbital (49). In order to examine the binding power of these orbitals, the 2σ is assigned two units of nuclear repulsion because it becomes the doubly occupied s orbital on fluorine in the separated atoms. This makes the 2σ orbital net binding by 0.141 units. The fluorine contribution to the 3σ orbital becomes a singly occupied p orbital and is assigned a nuclear repulsion of -1. Reference to Table IV shows that the penetration force due to the p character of the 3σ orbital comes close to balancing this repulsion. In addition, there is a large overlap force which makes the orbital net binding by 0.555 units. Thus the force analysis, which relates the strength of the binding not to the density itself but to the force exerted by the density, leads to the conclusion that the 3σ orbital is the one principally responsible for binding the proton

in hydrogen fluoride.

The density in the overlap region exerts 11 % of the total electronic force on the proton in the S.C.F. function, but the resulting penetration force is insufficient to provide a net zero force on the hydrogen nucleus. In the electrostatic function the overlap density exerts 7.8 % of the total electronic force, while the remainder is made up from density on the fluorine nucleus. It should be recalled that at infinite separation $P_H = 9.00$ and $O_H = 0.00$ in units of $1/a_0^3$. Thus in forming the molecule the proton penetrates the fluorine atom density to the extent that effectively only 8.3 of the nuclear charges are screened, but there is an accompanying transfer of density to the binding region which gives rise to the overlap force and hence to the formation of a stable molecule.

The field at the fluorine nucleus is given for the two densities in Table V. In the equivalent orbital notation ψ_b is the only orbital which contributes a penetration or an overlap force, and even in the symmetry orbital representation these binding forces are primarily located in the 3σ orbital. The magnitude of the overlap field is of some interest. It is twice as large as the field due to same overlap density at the proton,[1] and more than enough to balance the repulsive field due to the proton. In addition,

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1. This casts doubt on the validity of assigning half of the overlap population to each participating centre in obtaining gross atomic populations.

TABLE V.

Force on the fluorine nucleus in HF in units of $9/R^2$ a.u.

(i) Electrostatic density.

Orbital	Atomic force	Overlap force	Penetration force	Electronic force
γ_o	2.565	0.000	0.000	2.565
γ_b	-4.105	1.393	0.386	-2.326
γ_1	0.761	0.000	0.000	0.761
Total:	-0.779	1.393	0.386	1.000

(ii) Best limited S.C.F. density.

Orbital	Atomic force	Overlap force	Penetration force	Electronic force
1σ	0.078	-0.004	0.000	0.074
2σ	0.545	0.307	0.040	0.892
3σ	-2.740	1.349	0.443	-0.948
γ_1	-0.800	0.000	0.000	-0.800
γ_b	-1.395	1.656	0.483	0.744
Total:	-2.117	1.652	0.483	0.018

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there is a positive contribution from the density located at the hydrogen nucleus which alone would balance almost half of the repulsive field. The net result of bond formation is a positive field at the fluorine nucleus of about one unit, to be counterbalanced by charge polarization. In the S.C.F. density too much deformation occurs; the total atomic contribution is -2, which leads to a

total field just about equal to the repulsive field of -1 from the proton. This is overcome in the electrostatic density by the introduction of polarization in the inner shell orbital, which substantially reduces the total atomic contribution.[1]

The large negative atomic force in the S.C.F. density is at least partly due to the lone pair hybridization present. This results in a field of -0.8 in ψ_1, as opposed to +0.8 in the electrostatic density where the lone pair hybrids are pointing towards the proton. One method of reducing the unfavourable force on fluorine in the S.C.F. wave function would be to introduce configuration interaction with the 4σ state. The force on the fluorine nucleus can be calculated for an electron in this unoccupied molecular orbital and it turns out to be large and positive. In view of the earlier discussion of inner shell polarization, it is expected that configuration interaction involving the 1σ orbital will also help the system to attain electrostatic equilibrium. Finally, if an expanded basis set is employed, it would seem important to include a 'shrunken' 2p orbital on the fluorine atom.

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1. If a polarizing orbital of the same effective radius as the 1s orbital was used, the relative magnitude of the atomic contributions from ψ_b and from ψ_o would decrease considerably. It will be recalled that orthogonality requirements result in a decreasing atomic force in the bond orbital as p character is introduced into ψ_o.

Other molecular properties.

Many of the moments of hydrogen fluoride which can be compared to observed properties of the molecule have been calculated by Karplus and Lipscomb and co-workers (62, 63, 64). They found that wave functions which gave reasonable estimates of energies did not necessarily yield good estimates of these properties. A method of 'constrained' variation calculations was suggested by Karplus (5). In this approach it was required that the expectation values of certain operators agreed with the known values for the corresponding properties. It was hoped that the resultant increase in energy would be more than compensated for by an increase in the accuracy with which other one-electron operator functions could be calculated. The method was applied to hydrogen fluoride, by modifying the 'best limited' wave function obtained by Ransil. Karplus chose as constraining functions the dipole moment and the electric field gradient at the deuteron in DF. He found that the diamagnetic and paramagnetic contributions to the susceptibility were in better agreement with experiment; the calculated diamagnetic proton shielding decreased, but no accurate measurement is available for comparison; the force on the hydrogen nucleus approached closer to zero, but the force on fluorine increased. The significance of

his results is clear - for the first time it has been demonstrated that, starting with a given set of basis orbitals, that wave function which gives the best energy does not predict the best values of all other properties.

It was concluded from the anomalous value predicted for the force on the fluorine nucleus that 'considerably greater distortion of the fluorine atom wave function than that permitted by limitations in the basis set appears to be required'. However, the inner shell orbital was left unchanged in the constrained treatment on the grounds that a variation of its coefficients would result in a large increase in energy and only a small change in the dipole moment and field gradient. The present calculations indicate that the force on fluorine would greatly improve if such a variation was included.

It is possible to compare three wave functions using the same basis set of orbitals but derived under the following criteria:

(i) The minimum energy criterion of the variation method (Ransil);

(ii) The same, with the additional requirements that $\langle P_2/r_D^3 \rangle$ and $\langle P_1 r \rangle$ give the correct values (Karplus and Mukherji);

(iii) The criterion of electrostatic equilibrium, which requires $\langle P_1/r_H^2 \rangle$ and $\langle P_1/r_F^2 \rangle$ to be correct, with the dipole moment criterion of $\langle P_1 r \rangle$.

P_1 and P_2 are Legendre polynomials of the first and second degree.

The properties calculated from these functions are listed in Table VI. Two densities (which are listed in detail in Table I) are given for the electrostatic method to illustrate how the properties change with lone pair hybridization. On transforming the constrained function it is found that $\varepsilon_1 = 8.5^\circ$ compared to 0° and -6° for the best electrostatic densities. These latter three functions all have the correct dipole moment and therefore the same polarity of ~ 1.6, compared to a λ/μ of 1.38 for the Ransil function.

Forces and deuteron quadrupole coupling constant.

The forces for the electrostatic case are equal to or close to zero since they were used to fix the densities. The difference between the forces predicted by the other two functions can be explained in terms of the parameters describing them. Since more lone pair hybridization is predicted by the constrained function than by Ransil's, the force on fluorine increases. However, the force on hydrogen is more sensitive to the higher polarity than to this small increase in ε_1 and it consequently improves. The reason for this unfavourable change in the lone pair hybridization in the constrained function

can be found in the criterion of meeting the deuteron quadrupole coupling constant.

Kolker and Karplus (63) have discussed the contribution to this constant from different atomic orbitals on fluorine in relation to the corresponding nuclear contributions. They found that the 1s electrons exactly shield their share of charge while the $2p_\pi$ electrons only shield about two-thirds of the corresponding nuclear charge. Thus both the field and the field gradient at the nuclei, as measured by the forces and the quadrupole coupling constants respectively, are sensitive to the same parameters. The same factors tend to increase or decrease the electronic contribution to both the field and the field gradient at the proton. As the lone pair hybridization decreases (other factors being equal) both these quantities decrease. At $\varepsilon_1 = 8.5^\circ$ the calculated coupling constant reproduces the experimental value, but the force on hydrogen is too large; at $\varepsilon_1 = -6^\circ$ the force on hydrogen is correct, but the calculated coupling constant is lower than the experimental value. The chosen value of the deuteron quadrupole coupling constant is subject to experimental error and the calculated value is subject to an uncertainty in Q_D (63). Thus the deuteron quadrupole coupling constant would seem to be a less reliable criterion of the density distribution than that of electrostatic equilibrium.

TABLE VI

Properties of hydrogen fluoride

Property	S.C.F.[1] calculation	Constrained calculation	Electrostatic calculations $\varepsilon_1 = 0^o$	Electrostatic calculations $\varepsilon_1 = -6^o$	Experiment
Dissociation energy in e.v.	2.56	2.44	-	-	6.06 ± 0.2[2]
Dipole moment in Debyes	1.44	1.82	1.82	1.82	1.820 ± 0.003[3]
Diamagnetic susceptibility in e.m.u./mole[4]	-9.585×10^{-6}	-9.329×10^{-6}	-9.200×10^{-6}	-9.112×10^{-6}	-9.2×10^{-6}
Proton shielding constant[5]	3.11×10^{-5}	3.01×10^{-5}	2.98×10^{-5}	2.97×10^{-5}	-
Deuteron quadrupole coupling constant in kc/sec.[6]	372.2	339.9	306.0	284.0	340 ± 40
Force on fluorine in atomic units[7]	-2.944	-3.008	0.000	0.000	0
Force on hydrogen in atomic units	-0.084	-0.044	-0.018	-0.004	0

Table VI continued.

1. Apart from the deuteron quadrupole coupling constant, all moment results listed for the constrained function and for Ransil's function have been checked by an independent evaluation of integrals.

2. J.W.C. Jones and R.F. Barrow, Proc. Roy. Soc. (London) A251, 504 (1959).

3. R. Weiss, Abstracts of 6th Brookhaven Converence on Molecular Beams, June, 1962.

4. The diamagnetic contribution was calculated from the fluorine nucleus as origin. R.P. Hurst, M. Karplus and T.P. Das, J. Chem. Phys. 36, 2786 (1962) calculated the corresponding paramagnetic term from the results of M.R. Baker, C.H. Anderson, J. Pinkerton and N.F. Ramsey, Bull. Am. Phys. Soc., 6, 19 (1961), on the rotational magnetic moment of HF. The total susceptibility was measured by P. Erlich, z.f. anorg. und allgem. chem., 249, 219 (1942). Combining these leads to the 'experimental' value quoted.

5. The paramagnetic part of the shielding constant is -79.6 ± 0.5 p.p.m. as determined by S.I. Chan and T.P. Das, J. Chem. Phys., 37, 1527 (1962) from the spin rotational constants measured by N.F. Ramsey, Am. Scientist. 49, 509 (1961). The proton was taken as the origin for the diamagnetic part.

6. Q_D was taken as 2.82×10^{-27} cm^2, J.P. Auffray, Phys. Rev. Letters 6, 120 (1961). The experimental determination of the coupling constant of DF was made by H.M. Nelson, J.A. Leavitt, M.R. Baker and N.F. Ramsey, Phys. Rev., 122, 856 (1961).

7. The result for the force on fluorine for Ransil's function was slightly in error in the work of Karplus and Mukherji (5). The authors agree with the present value.

Diamagnetic susceptibility.

The diamagnetic contribution to the susceptibility of hydrogen fluoride (χ_d) is determined by $\langle r_F^2 \rangle$ and therefore by the density in the region of the proton, where r_F is large. Changes in hybridization of the fluorine atom would have little effect on this property. The factors which determine the density at the hydrogen nucleus are the polarity and the orbital exponent of the h orbital. A low polarity and a small orbital exponent both increase this density and, as a result χ_d. The first effect is illustrated by the results in Table VI. Both the constrained function and the electrostatic functions have the correct dipole moment and give very good estimates of χ_d. The S.C.F. density has a low polarity, as shown by the dipole moment, and predicts too large a value for χ_d. A considerably larger value is predicted by the 'best atom' orbitals (62) which have an exponent of 1.00 for the hydrogen orbital. It can be concluded from these susceptibility calculations that the electrostatic function with $\varepsilon_1 = 0$ gives the best representation of the density at hydrogen. However, the lack of an error estimate for the experimental determination detracts from the significance of the agreement with this particular point.

Proton shielding constant.

No accurate measurement of the proton chemical shift of gaseous hydrogen fluoride is available, due to experimental difficulties (65). The shielding constant of gaseous methane is 3.01×10^{-5} and that of unassociated hydrogen fluoride is within 2p.p.m of this value. The results given in Table VI indicate that the chemical shift is very small relative to methane. Perhaps this is the reason for the failure of Schneider and coworkers (65) to observe a signal due to gaseous HF relative to methane. Again the constrained density and electrostatic densities give very similar results while the S.C.F. density predicts a larger value. The latter can be attributed to the low polarity predicted by the energy calculation. Since the shielding constant is sensitive to the amount of density right at the nucleus (while the susceptibility is determined by that density in the general region of the proton) it is less sensitive to polarity than it is to choice of orbital exponent.

Dipole moment.

The importance of the polarity in determining molecular properties is apparent from these results, particularly if they are compared to those calculated from the simple 'Slater atom' and 'best atom' orbitals (62,63) which

predict very low dipole moments as shown in Table III. A wave function predicting the correct dipole moment for which the hydrogen orbital exponent has been optimized might be expected to always yield good estimates of the diamagnetic susceptibility and proton shielding constant. The field and field gradient are more sensitive than these properties to the details of the electron distribution on each nucleus, but still need an accurate estimate of the polarity to yield the correct results. The calculations of the molecular properties support the thesis that the forces and dipole moment provide a good test of the overall density distribution. A density satisfying these criteria should also yield good estimates of the other one-electron properties discussed above.

Calculation of molecular properties.

As Kolker and Karplus (63) pointed out, the deteron quadrupole coupling constant differs from all other observed quadrupole coupling constants because the density around the deuteron is symmetrical and does not contribute to the field gradient at that nucleus. The observed coupling between heavy nuclei and molecular charge distributions can be estimated with a fair degree of accuracy by simple models (66), since it is determined

mainly by the ratio of p orbital character along the symmetry axis to that perpendicular to this axis. No similar scheme can be applied to the deuteron coupling, which (like the force on the proton) is a 'delicate balance' between the electronic and nuclear contributions.

In a diatomic molecule the expectation value of q_β the field gradient at nucleus β, is given in atomic units by

$$q_\beta = 2\, Z_\alpha/R^3 \; - \; \langle \Psi^* | \sum_i [3\cos^2\theta_{i\beta} - 1]/r_{i\beta}^3 | \Psi \rangle$$

or more briefly by

$$q_\beta = 2\, Z_\alpha/R^3 \; - 2 \langle \Psi^* | \sum_i [P_2/r_{i\beta}^3] | \Psi \rangle$$

where P_2 is the normalized Legendre polynomial of order two. When the ground state wave function Ψ is expressed as a single determinant molecular orbital wave function this sum can be written as

$$q_\beta = 2\, Z_\alpha/R^3 \; - \; \sum_i 4 \langle \psi_i^* | P_2/r_\beta^3 | \psi_i \rangle$$

where the ψ_i are doubly filled orthonormal molecular orbitals.

The integrals arising when the molecular orbitals are expressed as a sum of atomic orbitals are troublesome due to the $1/r_D^3$ dependence. The penetration type integrals,

involving two orbitals on the fluorine nucleus, can be obtained from the general formulae of Pitzer, Kern and Lipscomb (67). The overlap type integrals can not be evaluated by the method of Barnett and Coulson (68) which is limited to r^n where $n \geq -1$. One alternative is to expand $1/r^3_D$ about the fluorine nucleus using Gegenbauer polynomials (69) and then to expand the exponential term describing the density at the deuteron. This is followed by a one centre integration. Another method is an integration in confocal elliptic co-ordinates (63) with due allowance for singularities arising at the nucleus. Kolker and Karplus (63) have demonstrated how this approach can readily be extended to machine computation.

The field gradient obtained in this way can be related to the measured coupling constant eqQ/h kc. per sec. If the deuteron quadrupole moment is taken to be $2.82 \times 10^{-27} cm^2$ the relationship is eq_DQ_D/h in kc./sec. = $663 \times q_D$ in atomic units. (5)

The <u>dipole moment</u> calculation for a diatomic molecule is straightforward. For a single determinant molecular orbital wave function it can be written as

$$D = Z_\beta R - \sum_i 2 \langle \psi_i^* | r_a \cos \theta a | \psi_i \rangle$$

in atomic units. It is most convenient to use the fluorine

nucleus as origin for the calculation since many of the terms are zero in this case. However, the overlap type integrals are best evaluated from the proton as origin since the resulting integrals can be checked to three figures in the tables of overlap integrals listed by Mulliken, Rieke and Orloffe, (70). This is possible because of the relationship $r_\alpha \cos\theta_\alpha + r_\beta \cos\theta_\beta = R$ which relates the overlap dipole calculated from the two centres. Analytical expressions are available for the overlap dipoles in the lists of Coulson (71) and (72) and the one centre integrals are listed in the appendix.

The proton magnetic shielding constant can be split into a paramagnetic and diamagnetic contribution in the perturbation theory developed by Ramsey (73). The diamagnetic part, σ_d, measures what the shielding would be if the whole electronic structure was free to rotate about the nucleus without interference from the other nuclei. Since it is a measure of the potential energy of the nucleus in the electric field of all the electrons, $\langle 1/r_H \rangle$, it can be evaluated from the ground state wave function of the molecule. Opposing σ_d is a large paramagnetic contribution, a measure of the magnetic field at the nucleus arising from the non-spherical potential about the proton. To calculate it requires a knowledge of the excited state wave functions of the molecule, but Ramsey (73) has shown how it can be

evaluated once the spin-rotational constants are known, either from molecular beam studies or from microwave spectroscopy. This calculation is possible because the electronic contribution to the spin-rotational interaction is also determined by the magnetic field at the nucleus due to the electronic rotation. Chan and Das (74) have calculated σ_p for all the molecules for which the spin-rotational constant has been measured.

The diamagnetic contribution to the proton shielding constant is given by

$$\sigma_d = e^2/6mc^2 \langle \Psi' | 1/r_H | \Psi \rangle \quad \text{or if } r_H \text{ is in atomic units,}$$

$$= \alpha^2/6 \quad \langle \Psi' | 1/r_H | \Psi \rangle$$

$$= 17.750 \times 10^{-6} \langle \Psi | 1/r_H | \Psi \rangle \ .$$

The sign is taken as positive here, since the paramagnetic contribution is smaller than the diamagnetic part and by convention in nuclear magnetic resonance spectroscopy the shielding constant is positive. The two centre integrals required for the calculation are listed in the appendix and are taken from the tables of Coulson (71). The only one centre integral arising is simply equal to the effective nuclear charge of the hydrogen orbital.

The total magnetic susceptibility for a molecule

is also composed of two terms when calculated by perturbation theory; the diamagnetic term χ_d and an induced paramagnetic or 'high frequency' term χ_p which arises from the non-central nature of the potential field in which the electrons move. (73,75). It is χ_d which contains the measure of $\langle r^2 \rangle$ that is of interest here and some independent determination of χ_p must be available in order to obtain χ_d from the measured susceptibility. This can be done through a determination of the rotational magnetic moment of a molecule, as a consequence of the fact that the magnetic moment arising from the rotational motion of a molecule is determined entirely by an induced paramagnetism which can be related directly to χ_p. The rotationally induced diamagnetic contribution is cancelled by the moment generated by the rotation of the rigid charge density. While the total susceptibility is invariant to the choice of origin employed in its calculation, the relative values of χ_d and χ_p are not independent of this choice. In general the value of χ_p calculated from the Zeeman splittings of the rotational spectra of molecules is referred to the centre of mass as origin since it involves moments of inertia. (76) The diamagnetic contribution must therefore be referred to this origin as well. This transformation may be accomplished as follows:

The rotational average of the diamagnetic susceptibility is given by

$$\langle \chi_d \rangle \text{ av.} = -(e^2/6mc^2) \sum_{i=1}^{n} 2 \langle \psi_i^* | r^2 | \psi_i \rangle$$

or if the integrals are evaluated in atomic units as in the present case,

$$\langle \chi_d \rangle \text{ av.} = -\frac{\alpha^2 a_o^3}{6} \sum_{i=1}^{n} 2 \langle \psi_i^* | r^2 | \psi_i \rangle .$$

The sign convention used is that of Ramsey (73). α here refers to the fine structure constant and a_o to the Bohr radius of the hydrogen atom. This expression can be rewritten in terms of the ground state wave function as

$$\langle \chi_d \rangle \text{ av.} = -\frac{\alpha^2 a_o^3}{6} [\langle \Psi^* | r_X^2 | \Psi \rangle + n \Delta R^2 - 2 \Delta R \langle \Psi^* | r_X \cos\theta_X | \Psi \rangle]$$

where ΔR is the distance in atomic units between nucleus X and the mass centroid of the molecule and n is the number of electrons in the system. The last term in the brackets is just the electronic contribution to the dipole moment, as calculated from the X atom.

Alternatively, the diamagnetic contribution can be calculated from the heavy nucleus and the paramagnetic part can be transformed to the same origin. This was done by

Kolker and Karplus (63) in their calculation of the susceptibility of hydrogen fluoride. The results given in Table VI are therefore referred to the fluorine nucleus as origin. The formula given above measures the molecular susceptibility. On multiplying by Avogadro's number to obtain the molar susceptibility the conversion factor becomes

$$\chi_d = 7.9209\ 10^{-7}\langle\Psi|r_F^2|\Psi\rangle$$

The integrals arising are listed in the Appendix.

The calculation of the <u>forces</u> is described in detail in the Appendix, where the explicit expressions for the forces exerted on both nuclei are given.

III. THE WATER MOLECULE.

It was shown in the case of hydrogen fluoride that the four parameters ε_0, ε_1, λ/μ and c_3 provided sufficient flexibility in the form of the wave function to attain electrostatic equilibrium, while simultaneously satisfying the dipole moment criterion. Calculations of the remaining one-electron density properties indicated that the predicted distribution was indeed a good representation of the electron density in hydrogen fluoride. In the water molecule the limited basis set of atomic orbitals has to meet even more stringent requirements, since there is an additional force component which is not zero by symmetry. This is the force on a proton perpendicular to the bond axis, denoted by $F_\perp$ in Figure 12. The other components are the force on a proton along the bond axis, $F_\parallel$, and the force on the oxygen nucleus along the symmetry axis, F_0. There is also a new orthogonality condition; a bond orbital must now be orthogonal to the lone pair orbitals and to the second bond orbital. As it transpires, the two extra conditions, one from the forces and the other from orthogonality, have to be used to fix two new parameters which were not required to describe the density in hydrogen fluoride. On including the delocalization

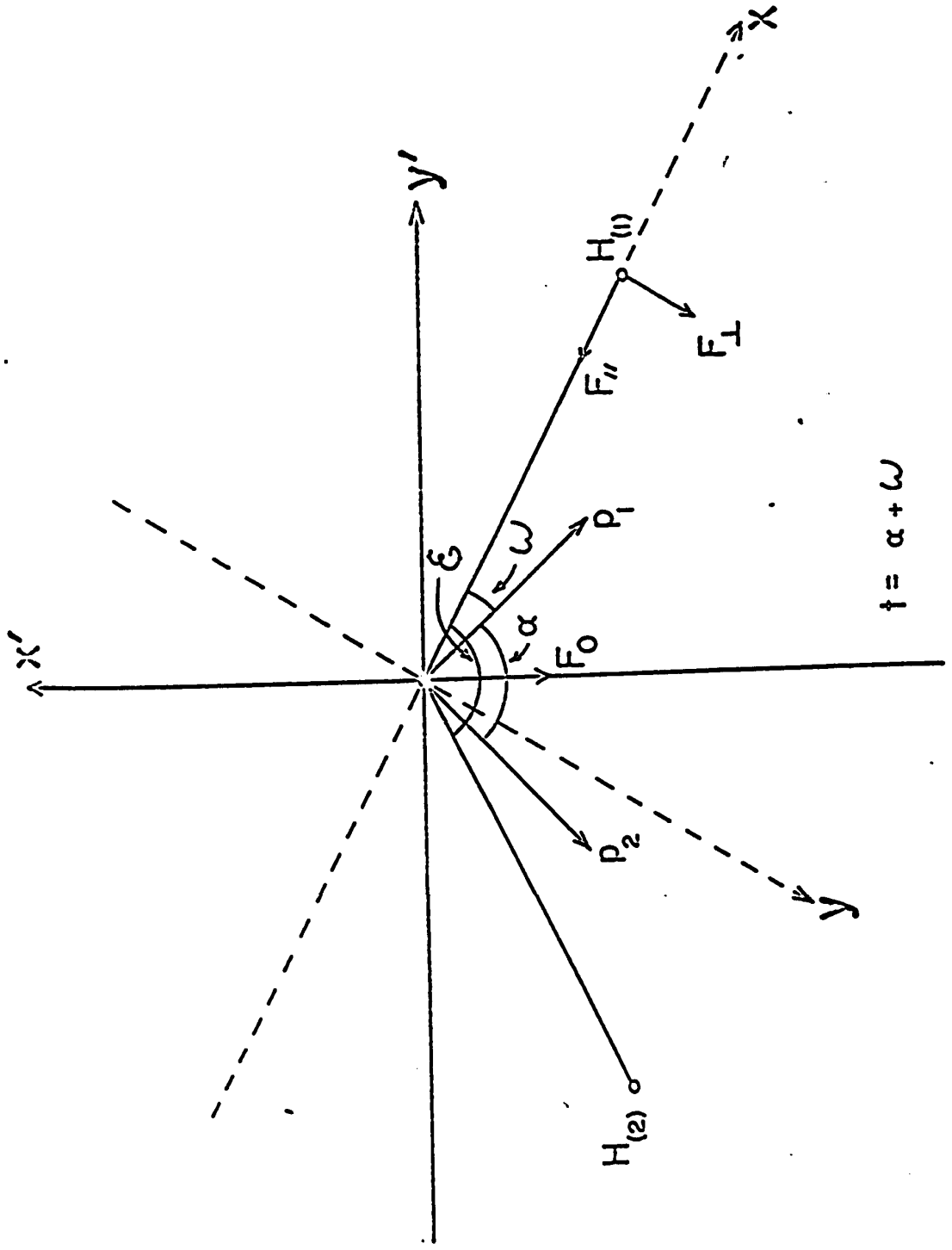

FIGURE 12. The coerdinate system used in the calculation of the density in the water molecule. The direction of positive force is indicated by arrows. The O-H and H-H distances are denoted by R and R_H.

parameter δ and allowing the bonds to 'bend' away from the bond axes, a total of six parameters is available to describe the density in the water molecule. Therefore the criteria of zero resultant forces in conjunction with the dipole moment, may be used to fit a relatively sophisticated density function to the known nuclear framework.

Choice of basis orbitals.

The electron density distribution is determined within the framework of the single configuration L.C.A.O. molecular orbital theory. As in hydrogen fluoride, the equivalent orbital representation is used to enable one to discuss lone pair and bond orbitals. Ellison and Shull have shown how the equivalent orbitals can be transformed from the symmetry orbitals (77). All the calculations were carried out for a bond length of 1.810 a.u. and a bond angle of 104.45° (78). Slater atomic orbitals were employed with the free atom orbital exponents, since no optimized exponent calculations have been performed. For the oxygen 2s and 2p orbitals the exponent was 2.275 and for the 1s orbital on oxygen, 7.700.

All available evidence points strongly against taking the free atom exponent of 1.00 for the hydrogen orbital (79,80,81). A much better approximation to the

true exponent is provided by the empirical rule discussed by Bader (12) which relates the screening in the separated atom to that in the united atom. By this rule $\zeta = Z_s - \Delta Z e^{-R}$ where $\Delta Z = Z_s - Z_u$. The Z_s and Z_u refer to the effective nuclear charges calculated by Slater's rules (including the factor 1/n where n is the principal quantum number) for the electron in the separated and united atom respectively. This yields a value of 1.34 for the proton in hydrogen fluoride compared to 1.32 obtained by Ransil (4) when the exponents were optimized. For the proton in water the exponent is calculated to be 1.32 and for ammonia, 1.29. The results of Ransil indicate that these values, which are used in the force calculations, may be too large by $\sim$0.2 units. This is only likely to affect a comparison between the three types of bonds which is based on a property very sensitive to the exponent, such as the shielding constant. Both the formula and the results of variation calculations (4) indicate much smaller changes in the exponents of the heavy atom orbitals on bond formation compared to that of the hydrogen orbital. Some of the calculations were repeated using these slightly different heavy atom exponents with no significant change in the results.

It is assumed that the inner shell electrons are in a pure 1s orbital initially, i.e. the parameter $c_3 = 0$,

and that the 1s character in the valence orbitals is determined by 2s-1s orthogonality. Therefore the oxygen s orbital which will be used is the orthogonal 2s orbital $s = (1 - S^2)^{-\frac{1}{2}}(s' - S\ 1s)$ where s' is the nodeless Slater orbital and S is the overlap integral between s' and 1s. Due to practical difficulties it is necessary to ignore the non-orthogonality between the 1s of the inner shell and the hydrogen orbitals in the valence shell. As shown in hydrogen fluoride, this will lead to a relatively good value of the force on oxygen but will hardly affect other parameters. Hence not much significance can be attached to the absolute value of the force on oxygen, although its dependence on molecular parameters will not be vitiated. The most general orbitals that can be written for the water molecule are now

$$\psi_{b1} = \lambda[\cos\varepsilon_b\ s + \sin\varepsilon_b\ p_1] + \mu[h_1 - \delta h_2]$$

$$\psi_{b2} = \lambda[\cos\varepsilon_b\ s + \sin\varepsilon_b\ p_2] + \mu[h_2 - \delta h_1]$$

$$\psi_{l1} = \cos\varepsilon_1'\ s + \sin\varepsilon_1'\ p_3$$

$$\psi_{l2} = \cos\varepsilon_1'\ s + \sin\varepsilon_1'\ p_4$$

The h_1 and h_2 denote 1s orbitals on $H_{(1)}$ and $H_{(2)}$ respectively and the p_i are 2p atomic orbitals centred on the oxygen nucleus. The directions of p_1 and p_2 are

shown in Figure 12 (they do not necessarily coincide with the bond axes) and p_3 and p_4 determine the directions of the equivalent lone pair orbitals. As in the case of hydrogen fluoride, it is convenient to replace the two equivalent lone pair orbitals by one $2p_\pi$ orbital and one hybrid orbital along the symmetry axis. This hybrid can be written

$$\psi_1 = \cos\varepsilon_1 \, s + \sin\varepsilon_1 \, p_{x'}.$$

The two lone pair hybridization parameters are easily related:

$$\cos\varepsilon_1' = (1/\sqrt{2}) \cos\varepsilon_1 \qquad \text{and}$$

$$\sin\varepsilon_1' = (1/\sqrt{2}) \sin\varepsilon_1/\cos(\beta/2)$$

where β is the angle between the equivalent orbitals, given by $\cos\beta = -\cot^2\varepsilon_1'$.

These orbitals embody five parameters:

(1) ε_1 determines the lone pair hybridization of an orbital along the symmetry axis with limiting character s and sp^2. The corresponding equivalent orbitals go from sp to sp^3.

(2) ε_b is the bond hybridization, exactly analagous to the corresponding parameter in hydrogen fluoride.

(3) λ/μ again measures the bond polarity.

(4) α, the angle between the p functions of the bond

orbitals. It is termed the orbital angle as opposed to the bond angle ε. When $\alpha \neq \varepsilon$ the bonds are termed 'bent'. (5) δ, the parameter which determines the extent of delocalization of the equivalent orbitals. The requirement of mutual orthogonality between the orbitals can be used to fix two of these five parameters. The condition that the equivalent lone pair orbitals be orthogonal was used to obtain the expression relating the angle between these orbitals to the hybridization.

From the conditions that (i) $\int \psi_{b1}\, \psi_{b2} d\tau = 0$ and (ii) $\int \psi_{b1}\, \psi_{l} d\tau = 0$ one obtains the equations

$$\text{(i)}\quad (\lambda/\mu)^2 \left[\cos^2\varepsilon_b + \sin^2\varepsilon_b \cos\alpha\right] + 2\lambda/\mu \left[S_2 \cos\varepsilon_b(1-\delta) + S_3 \sin\varepsilon_b (\cos t - \delta\cos\omega)\right] + \left[S_1 (1+\delta^2) - 2\delta\right] = 0$$

$$\text{(ii)}\quad \tan\varepsilon_1 = \frac{S_2(1-\delta) + \lambda/\mu \cos\varepsilon_b}{S_3 \cos(\varepsilon/2)(1-\delta) + \lambda/\mu \sin\varepsilon_b \cos(\alpha/2)} = \tan\varepsilon_1' \cos(\beta/2)$$

The requirement of normalization of the bond orbitals allows one to determine the absolute values of λ and of μ once their ratio is known. This condition is

$$(iii)\quad \mu^2[1 + \delta^2 - 2\delta S_1 + 2\lambda/\mu\{S_2\cos\varepsilon_b(1-\delta) + S_3\sin\varepsilon_b(\cos\omega - \delta\cos t)\} + (\lambda/\mu)^2] = 1$$

The remaining three parameters can be fixed by the requirement of zero resultant forces or by fixing two forces and the dipole moment. The parameters, forces and dipole moment were programmed for machine computation as follows. For a particular choice of λ/μ, α and δ the parameter ε_b is obtained from equation (i)[1]. Equation (ii) was then used to obtain ε_1 and equation (iii) to calculate λ and μ. Further details of the calculations are given in the Appendix.

Determination of density distribution.

Since the orbitals are mutually orthogonal and doubly occupied, the electron density is

$$\rho = 2(\psi_{b1}^2 + \psi_{b2}^2 + \psi_1^2 + \psi_\pi^2 + \psi_o^2)$$

where ψ_o is the innermost orbital of the oxygen atom.

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1. Equation (i) as it stands can be solved by a trial and error method. Since ε_b is $(90^\circ+m)$ where m is less than 15°, $\cos\varepsilon_b$ and $\sin\varepsilon_b$ can be expanded in terms of m. Retaining terms to the order of m^2 converts equation (i) into a quadratic expression in m. This method and equation (i) give identical results well within the accuracy required. As an example, for $\delta = 0.3$, $\lambda/\mu = 1.4$ and $\alpha = 70.00^\circ$, both methods give $\varepsilon b = 95.87^\circ$.

The Hellmann-Feynman theorem enables one to write down the total force acting on any nucleus in the molecule as the sum of the repulsions due to the other nuclei and the electronic forces exerted by the above distribution. If $F_\perp$, $F_\parallel$ and F_0 refer to the electronic forces only, the three conditions for electrostatic equilibrium are

$$F_\perp = F_\perp(\varphi_{b1}^2) + F_\perp(\varphi_{b2}^2) + F_\perp(\varphi_1^2)$$

$$= (1/R_H^2) \cos(\varepsilon/2)$$

$$F_\parallel = F_\parallel(\varphi_{b1}^2) + F_\parallel(\varphi_{b2}^2) + F_\parallel(\varphi_1^2) + F_\parallel(\varphi_\pi^2) + F_\parallel(\varphi_0^2)$$

$$= (8/R^2) + (1/R_H^2) \sin(\varepsilon/2)$$

$$F_0 = 2F_0(\varphi_b^2) + F_0(\varphi_1^2)$$

$$= (16/R^2) \cos(\varepsilon/2)$$

Where no distinction is made between the forces exerted by φ_{b1} and φ_{b2} the two forces are equal, and any terms that are zero are not shown. Explicit expressions for all of the forces are given in the Appendix. Three sets of density functions will be considered, from the simplest embodying only ε_b, ε_1 and λ/μ to one including all five parameters. Each distribution will be regarded in the light of whether or not it can simultaneously satisfy all three of the zero

force conditions and predict the correct dipole moment, of magnitude 0.724 a.u.

Case I. Equivalent localized orbitals directed along the O-H bond axes.

The set of orbitals with $\alpha = \varepsilon$ (bonds pointing at the hydrogen atoms) and $\delta = 0$ (completely localized equivalent orbitals) is the simplest that one can construct for the water molecule. If ε_b and ε_1 are determined by the orthogonality conditions only one parameter, λ/μ, remains to be fixed by any of the force conditions or by the dipole moment. Pople and Duncan (43) used the latter criterion to obtain a density function, which can be examined in terms of the forces exerted by it on the nuclei.

Since the bond orbitals are directed at the hydrogen atoms, the order of hybridization is automatically fixed. A variation of λ/μ brings about only small variations in ε_b and ε_1' e.g. as λ/μ increases from 1.0 to 1.5, ε_b decreases from 79° to 73° and ε_1' changes from 56.0° to 56.5°. Thus the lone pairs are always dominant in this case as ε_1' is fixed close to 60°, the value for sp^3 orbitals. The correct dipole moment is obtained at $\lambda/\mu = 1.07$ with $\varepsilon_b = 77.8°$ and $\varepsilon_1' = 56.0°$.[1] Since all the factors vary

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1. These values for λ/μ, ε_b and ε_1' are slightly different to those obtained by Duncan and Pople (1.06, 85° and 55° respectively) since they used a hydrogen orbital exponent of 1.00.

so little with λ/μ in this case, it will be sufficient to consider the forces obtained for this one point. They are given in Table VII.

TABLE VII.

Orbital contributions to the forces in Case I for H_2O.

	$F_\perp$	$F_\parallel$	F_C
$F(\psi_{b1}^2)$	0.0000	0.6812	3.8760
$F(\psi_{b2}^2)$	0.1206	0.3058	3.8760
$F(\psi_1^2)$	-0.1046	0.3564	-7.5568
$F(\psi_\pi^2)$	0.0000	0.4556	0.0000
$F(\psi_c^2)$	0.0000	0.6105	0.0000
Electronic force	0.0160	2.4095	0.1952
Nuclear repulsion	-0.0748	-2.5384	-2.9920

It is clear that this simple density distribution does not come close to satisfying the conditions of zero resultant forces. Since the electron distribution in ψ_{b1} possesses axial symmetry along the $O\text{-}H_{(1)}$ bond axis it exerts no force perpendicular to the bond. The density in ψ_{b2} attracts $H_{(1)}$ but the lone pairs exert a force in the opposite direction, tending to open up the bond angle, which almost cancels the attractive force of ψ_{b2}. The

resultant electronic attractive force F_1 is thus very much less than the nuclear force of repulsion. The case of the forces acting on the oxygen nucleus is very similar to that for F_1. The lone pairs exert a force which is almost equal and opposite to the attractive forces of the bond electrons. The result is a large negative force acting on the oxygen nucleus almost equal to the total nuclear force of repulsion. The electronic force on $H_{(1)}$ along the bond F_H is also insufficient to overcome the repulsive force. This again is mainly due to the decrease in $F(\psi_1^2)$ from 0.54 for a pure 2s orbital to 0.36 for the hybridized orbital.

Projection of the lone pair electron density out to the back of the molecule in these methane-like orbitals results in unreasonably large forces tending both to pull the oxygen atom back and to open up the bond angle. Such a distribution is also unsatisfactory in terms of bond moments. In order to meet the dipole moment with such a large contribution from the lone pair electron (1.24 a.u. compared to a total dipole moment of 0.72 a.u.), the bond moment is O($\delta+$) - H($\delta-$), in contradiction to chemical intuition and experience, e.g. hydrogen bonding. It is clear that in order to attain an equilibrium distribution the prominence of the lone pair electrons has to be greatly reduced.

Case II. Localized equivalent orbitals with bent bonds.

As the angle between the two hybrid bond orbitals decreases, their p character increases and the equivalent lone pair orbitals approach sp hybrids. If no hydrogen atoms were present the bond orbitals would be pure p orbitals ($\varepsilon_b = 90^\circ$) when the lone pairs reached this limit ($\varepsilon_l' = 45^\circ$). Overlap with the hydrogen orbitals increases the p character of the bond orbitals and decreases the s character of the lone pair orbitals, for a particular value of the orbital angle. Consequently the lone pair orbitals actually attain their limiting form for an orbital angle smaller than 90°. The corresponding bond orbitals are no longer pure p bonds due to appreciable overlap of the hydrogen with the s in the lone pairs. To retain orthogonality the bond orbitals must contain negative s.

The limiting value of the orbital angle is determined by the requirement that the two orthogonality conditions (i) and (ii) possess real solutions for ε_b and ε_l. The limiting value of ε_l so obtained is always very close to 0°, unlike the case of hydrogen fluoride where ε_l can become increasingly negative. Results for this case are plotted in Figure 13. It shows the variation with α of the orbital contributions to the perpendicular force on the hydrogen nucleus, for $\lambda/\mu = 1.45$. This

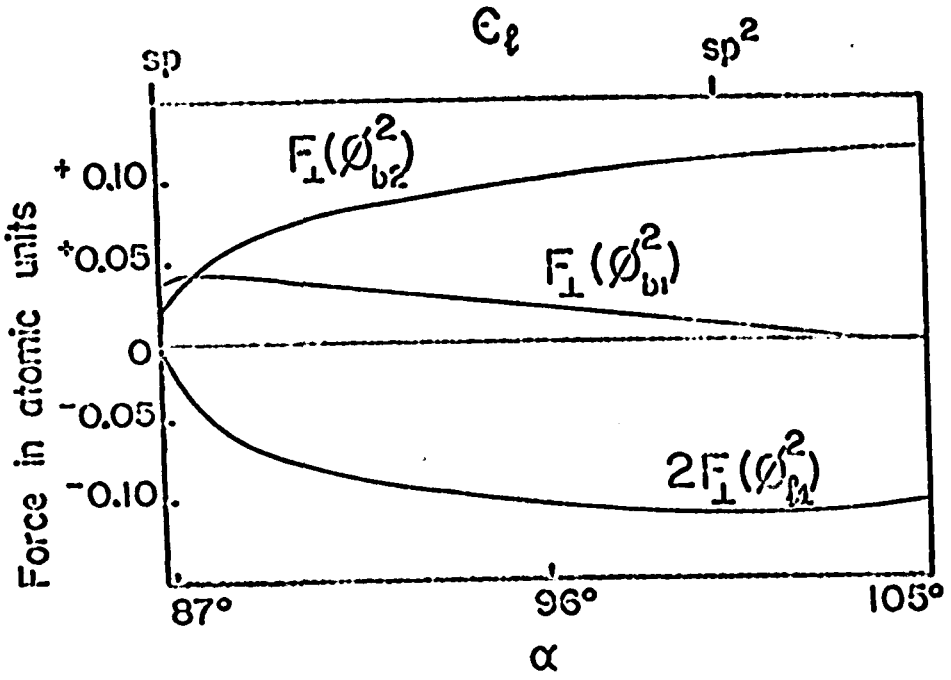


FIGURE 13. The orbital contributions to the force on a proton perpendicular to the bond axis in the water molecule as the bonds are bent (Case II). The scale for ϵ_1 given at the top of the figure is not a linear one.

polarity is chosen since it reproduces the dipole moment at $\alpha = 87^{\circ}$ where the predicted forces are best. (The increased bond polarity is necessary to compensate for the loss of the lone pair atomic dipole). All the orbital contributions to the force vary in a regular manner. The lone pair orbitals exert a steadily decreasing force as the bonds are bent; in the limit of sp hybridization they project out above and below the plane of the molecule at right angles to the bonds and exert no force. $F(\psi_{b2}^{2})$ decreases as the bonds are bent due to the decreasing amount of s in ψ_b. For every value of α this contribution just cancels that due to the lone pairs, as in Case I. This means that the whole nuclear repulsion has to be counterbalanced by the force on the nucleus due to the density placed alongside the bond in ψ_{b1}. The maximum attractive force, of magnitude 0.04814 a.u., is attained at $\alpha = 87^{\circ}$, but it is insufficient to balance the nuclear repulsion of -0.07482 a.u. Exactly the same considerations apply to the force on the oxygen nucleus. Here the best force is 2.041; while this represents a great improvement over the value obtained with $\alpha = \varepsilon$ the net force is still -0.992. The electronic force exerted on hydrogen along the bond axis is increased to 2.518 a.u. due to the increased shielding by the lone pair electrons. This net force is decreased to only -0.020 a.u.

Introducing bent bonds has therefore brought the water molecule much closer to electrostatic equilibrium. In order to balance the remaining forces it is necessary to bend the bonds even more before the lone pair orbitals reach their limiting form. It will also be a help if the amount of negative s introduced into the bonding orbitals is reduced (here ε_b is 107.6° in the limiting case). Both of these aims can be achieved by delocalizing the bond orbitals.

Case III. Delocalized equivalent orbitals with bent bonds.

It is well known (77) that the exact transformation of a set of molecular orbitals into the corresponding equivalent orbitals will not in general result in completely localized bonding orbitals. Although it was at one time hoped that the amount of delocalization or mixing of the components of different bond orbitals would be negligibly small this has not proved true in known cases. It will be shown that it is of crucial importance in the description of the water molecule. The delocalization in this case requires the introduction of the h orbital of $H_{(2)}$ into ψ_{b1} and of the h orbital of $H_{(1)}$ into ψ_{b2}. The amount of delocalization is designated by δ as shown in the general expressions for ψ_{b1} and ψ_{b2}.

Introduction of delocalization into the bonding orbitals has a very pronounced effect upon the electron

density distribution. The overlap between the two hydrogen atoms is reduced from S_1 to $[S_1 (1+\delta^2) - 2\delta]$ which permits them to approach more closely and therefore allows the angle between the orbitals to decrease. The Pauli exclusion principle, as embodied in the condition of orthogonality, places a definite limit on the possible proximity of two orbitals made up of components with finite overlap. Another important effect of delocalization is to reduce the overlap between the oxygen s and p orbitals and the hydrogen atoms. As a result less negative s must be introduced into the bond orbitals to maintain orthogonality with the lone pair s orbital in the limiting case. e.g. with $\delta = 0$, the lone pairs reach their limit at $\alpha = 87^\circ$ with an ε_b of 108°, while at $\delta = 0.5$ this situation occurs at $\alpha = 59^\circ$ with an ε_b of 98°.

With the extra flexibility provided by this parameter a density distribution can be found which gives the correct dipole moment and comes very close to predicting zero forces on the proton. It will be recalled that three conditions are recuired to fix all the parameters in this case, the other two being used up in determining the orthogonalities. Table VIII shows the effect which the introduction of δ has on the forces and parameters. All of the forces listed are calculated from density distributions which have the correct dipole moment.

TABLE VIII.

Forces and parameters for Case III densities in H_2O.

δ	$F_\perp$	$F_\parallel$	F_0	α	λ/μ	ε_b	ε_1'
.40	0.0676	2.516	2.528	63.75°	1.479	100.59°	45.00°
.45	0.0690	2.512	2.576	61.30°	1.495	99.58°	45.00°
.50	0.0704	2.510	2.608	59.00°	1.514	98.55°	45.00°
.60	0.0720	2.506	2.656	54.95°	1.563	96.44°	45.00°
*	-0.0746	-2.538	-2.992	-	-	-	

* The final line lists the values of the nuclear repulsions opposing each of the electronic forces.

The forces $F_\perp$ and F_0 increase with increasing values of δ. $F_\parallel$ passes through a maximum in the region $0.35 < \delta < 0.40$, but changes slowly with increasing δ. This inability to achieve final electrostatic equilibrium makes it difficult to decide on a value for δ (one close to 0.5 is indicated), but the values of the remaining parameters can be specified within small bounds. The bond hybridization ε_b will be within a few degrees of 98° which indicates that the bond orbitals are essentially p bonds, with only 2% negative s character. The best forces are always obtained when the ecuivalent lone pairs are in sp hybrid orbitals directed above and below the

molecular plane. This orbital picture is close to that obtained from a qualitative use of valence bond theory, except of course that this distribution is for a bond angle of 104.45° and not the 90° molecule predicted by valence bond theory. The orbital angle of about 59° corresponds to an angle ω between the bond direction and the orbital direction of 22°. The bond polarity is 1.5, smaller than that in hydrogen fluoride as would be expected on the basis of electronegativity of the heavy atom. By concentrating density along the symmetry axis the polarity required to meet the dipole moment is decreased relative to that predicted by the simple valence bond approach.

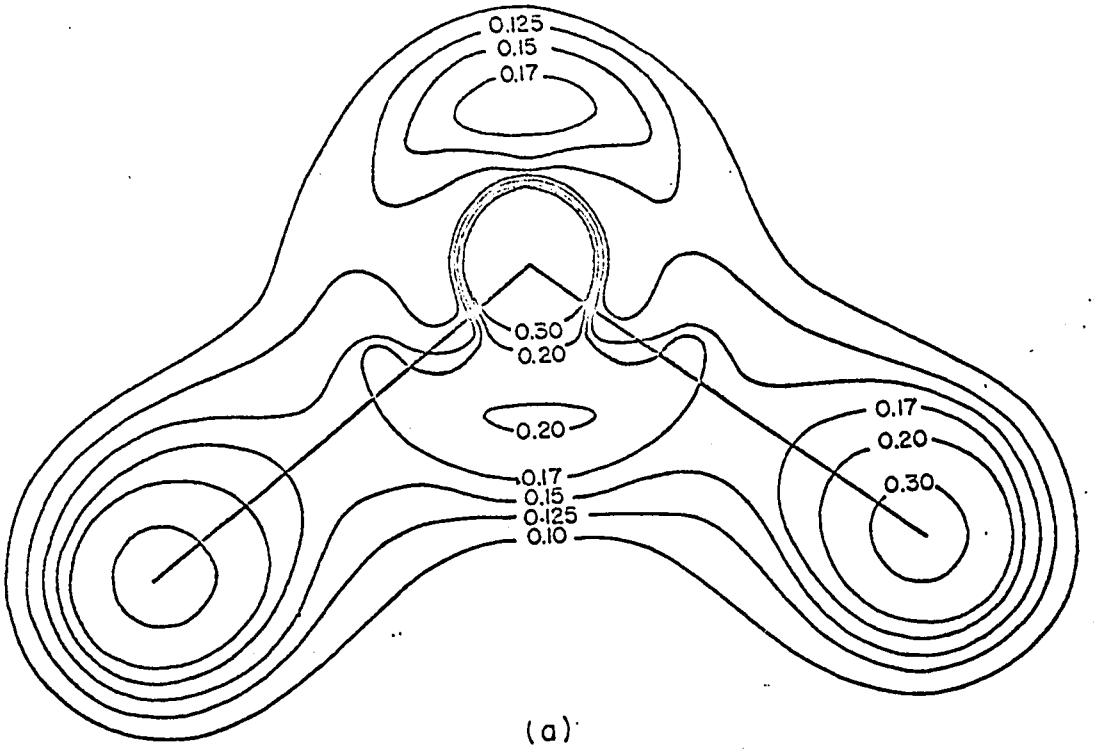
The remaining discrepancy in the force on the oxygen atom can be removed, as in the case of the hydrogen fluoride, by introducing p character into the inner shell orbital. A coefficient c_3 of 0.0044 is sufficient to meet this force provided the 1s - h overlap is ignored; inclusion of this non-orthogonality is estimated to increase the amount of p required by a factor of ten. Since even this order of inner shell polarization affected only the atomic force terms in hydrogen fluoride, the complete six parameter treatment was not attempted in the present case. The remaining forces on hydrogen correspond to those encountered in an O-H bond compression of 0.02A° and to a change in the bond angle of

1.5°. Additional polarizing orbitals representing the density on the fluorine and hydrogen atoms are no doubt necessary to account for these differences.

Comparison of density distributions.

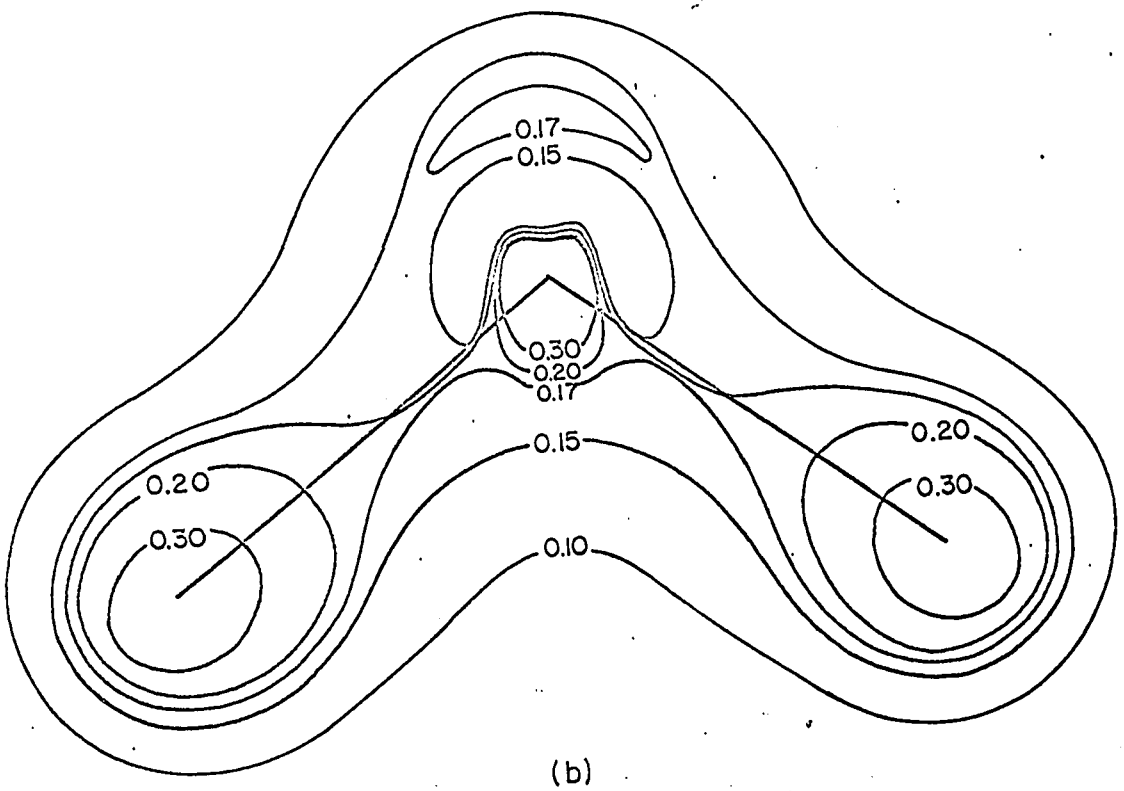
The most radical difference between the electrostatic electron density distribution and that proposed by Duncan and Pople is the decrease in prominence of the lone pair electrons. The lone pair orbitals according to the above authors are sp^3 in character, as opposed to the sp hybrids found in the present work. These electrons do not make any contribution to the dipole moment in the latter case as compared to their over-riding importance in determining the dipole moment when in sp^3 orbitals. As a result the electrostatic density predicts a much larger bond polarity than does the density of Pople. The present results agree with earlier views which attributed the dipole moment of the water molecule to the polarity of the bonds.

Some of the salient features of these two distributions are illustrated by the density contour maps in Figure 14. These represent lines of constant density due to the valence electrons in the plane of the water molecule. The upper diagram is for the best electrostatic density with $\delta = 0.5$ (the orbital coefficients and details of the method of calculation are given in the Appendix) and the lower



(a)

Case III density



(b)

Case I density

FIGURE 14. Density contour maps in a.u. of the valence electrons in the plane of the water molecule by (a) the electrostatic method, and (b) the method of Duncan and Pople.

diagram is for the Case I density defining a density of the type predicted by Pople and Duncan. The low polarity in Case I is reflected in the increased concentration of density at the protons. However the most striking difference lies in the concentration of charge above the oxygen nucleus when the lone pairs are prominent and below the oxygen nucleus when the bonds are permitted to bend. The large asymmetry in the oxygen density exhibited in (b) gives rise to very unbalanced forces on all three nuclei which would tend to pull the molecule apart. Distribution (a) accumulates this charge between all three nuclei where it can exert the maximum binding force. It also serves to maintain a spherical symmetry in the distribution surrounding the oxygen nucleus. As in the case of hydrogen fluoride, there is likely to be a large rearrangement of density when inter-molecular interactions occur. In ice, the maximum binding force will be obtained if the protons lie along tetrahedral directions from the oxygen nucleus. The force on this nucleus due to the two protons belonging to the molecule is opposed by the force due to the other two protons, so now the oxygen nucleus may well attain electrostatic equilibrium with a methane-like distribution. Thus structure (b) in Figure 14 is probably a good description of the electronic structure of a water

molecule in ice or in the liquid phase.

No variation calculations comparable in accuracy to those performed for hydrogen fluoride have been reported for the water molecule, due to the increased complexity of the system.[1] Ellison and Shull (77) performed an S.C.F. calculation using Slater orbitals with the free atom exponents. They investigated the effect of inner shell - outer shell mixing, concluding that it had a large effect on the wave function, and performed a limited configuration interaction calculation. McWeeny and Ohno (82) repeated these calculations and showed that the effect of inner shell mixing was greatly reduced when the h-ls orthogonality was taken into account. They performed a valence bond calculation, using the same integrals, and obtained an energy as good as that from the S.C.F. approach with limited configuration interaction. However, Slater (83) has reported that both of these results can only have qualitative significance due to approximations employed to obtain the three centre integrals. The results of the valence bond approach are not as good as they appeared to be.

Bearing in mind these qualifications regarding the density obtained by Ellison and Shull, one can examine the overall density characteristics predicted by their S.C.F. calculation. Their results predict an equilibrium bond

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1. It is worth noting that the force calculation for water is only complicated by the appearance of a few three centre integrals, more amenable to calculation than the energy integrals because they involve one-electron operators.

angle of 120°, a dipole moment which is too low by 0.5 Debyes and a binding energy 77% of the observed value at the correct bond angle. They transformed the single determinant wave function found for a bond angle of 105° into equivalent orbitals. The calculated bond orbitals did not lie along the bond axes and were not completely localized. Ellison and Shull were possibly the first workers to prove that hybridization may not be directly related to bond geometry in a polyatomic molecule. Their orbital angle was 69° compared to the 59° found in the present calculations. The bond orbital was mainly p, with a very small amount of negative s, and the equivalent lone pair orbitals were closer to sp than to sp^3. Their a_1' was in fact 47° compared to 45° in the electrostatic function. Thus the results of the energy calculation are far removed from the qualitative idea of tetrahedral bonds in the water molecule; extensive delocalization and bond bending is predicted in the bond orbitals, and little hybridization in the lone pair orbitals.

Even with this small amount of lone pair hybridization, Ellison and Shull were unable to achieve an energy minimum at the correct bond angle. The total energy was found to change extremely slowly with change in the bond angle, with the minimum occurring around 120°. At this angle the nuclear repulsion on a proton, perpendicular to the bond

axis, is 0.0508 a.u. and the predicted electronic force is 0.0548 a.u., which indicates that the true minimum occurs at an angle slightly less than 120°. Unlike the energy, this force is very sensitive to the bond angle and could be of help in locating the energy minimum in a variation calculation. At this predicted equilibrium position the electronic force on the oxygen nucleus is the difference between a positive force of 5.69 a.u. from the bond orbitals and a negative force of 4.34 a.u. from the lone pair orbitals. The resulting force of 1.35 a.u. has to balance a nuclear repulsion of -2.44 a.u. As in the case of hydrogen fluoride, this S.C.F. wave function therefore predicts a poor result for the force on the heavy nucleus.

Diamagnetic susceptibility.

The paramagnetic contribution to the susceptibility of water in the vapour phase has been determined from spectral data (76) to be 1.46×10^{-6} e.m.u./mole. No experimental measurement of the total susceptibility of water vapour appears to have been made, although the values for ice and liquid water are well known. Since the susceptibility is known to be fairly independent of phase (84) χ is taken to be -13.0×10^{-6} e.m.u./mole which is the value for the liquid. This yields an 'experimental'

$$\chi_d = -14.46 \times 10^{-6} \text{ e.m.u./mole.}$$

The electrostatic function with $\delta = 0.5$ predicts $\langle r_0^2 \rangle = 16.867$. On transforming this to the centre of mass as origin, the susceptibility becomes

$\chi_d = -16.650 \times 7.9209 \times 10^{-7} = -13.19 \times 10^{-6}$ e.m.u./mole.

Banyard (85) has calculated χ_d for a central field wave function and for that obtained by Ellison and Shull. From his work,

χ_d (central field wave function) $= -12.5 \times 10^{-6}$ e.m.u./mole

χ_d (Ellison and Shull) $= -15.2 \times 10^{-6}$ e.m.u./mole

As in the case of hydrogen fluoride, these results can be understood from a consideration of the factors affecting the distribution around the proton. The low polarity in the density of Ellison and Shull will tend to increase $\langle r^2 \rangle$, as will the small value of the orbital exponent ($\zeta = 1.00$) used for the h orbital. The susceptibility predicted by this density is larger than the experimental value. The electrostatic density has the correct dipole moment and therefore polarity, but as mentioned earlier the orbital exponent of 1.32 almost certainly overestimates the contraction of density at the proton. The slightly low value predicted for χ_d can be accounted for on this basis. Finally, the central field function is known to be too contracted in the region of the proton since it is based

on a one-centre expansion from the fluorine nucleus (65). This leads to a χ_d one unit lower than the electrostatic value. Das and Ghose (86) obtained the same value as the central field wave function, using a simple localized description of the bonds in water based on considerations of percentage ionic character. The predicted dipole moment was 3.1D, much larger than the experimental value of 1.84D, which could only be obtained by a very polar bond. The susceptibility is therefore low, in spite of an orbital exponent of unity which would tend to increase the total. This illustrates the danger of judging a density solely on one isolated criterion. In the case of the susceptibility, a combination of a low orbital exponent and high polarity factor may give very reasonable estimates of this property.

Proton magnetic shielding constant.

Das and Ghose have calculated the proton shielding constant from their wave function and from that of Ellison and Shull (86). The very low results found for the shielding constant in both cases contributed to the belief that simple S.C.F. wave functions do not give a good estimate of this property. This is contrary to the conclusion arrived at in the present work, that this property is determined almost exclusively by the orbital exponent. When a detailed

comparison of the orbital contributions for a proton in ψ_{1s} is made, as in Table IX, it transpires that they omitted the inner shell contribution to the shielding.[1] If this is added on, the calculated values of σ_d become 9.652×10^{-5} for the density of Das and Ghose, and 9.154×10^{-5} for the S.C.F. density. These are both based on an orbital exponent of unity and are consequently smaller than the electrostatic value of 10.606×10^{-5}. It can be seen from Table IX that the orbital contributions are consistently larger for the electrostatic density as a result of the increased h orbital exponent. The fact that Ellison and Shull's wave function yields a lower σ_d than does the highly polar density of Das and Ghose is surprising.[2] In general it is found that, for the same orbital exponent, the predicted shielding constant decreases as the polarity increases since charge is removed from the proton. This is the only example where this reasoning does not seem to apply.

Unfortunately there is no experimental determination of the spin rotational constant of water vapour and consecuently no available measure of σ_p. However, Chan and Das (74) have shown how, by suitable choice of

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1. The authors have agreed that this is the cause for the low values predicted (private communication).

2. This puzzled the authors as well; they feel that perhaps other factors such as hybridization are important here (private communication).

TABLE IX.

Orbital contributions to the proton magnetic shielding constant in H_2O.

Density	γ_{b1}	γ_{b2}	γ_1	γ_π	γ_o	Total	$\delta_d \times 10^5$
Das and Ghose(66)	1.624	0.883	0.848	0.977	?	4.332	7.69
Electrostatic	1.776	0.996	1.089	1.008	1.105	5.974	10.61

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origin, σ_p can be estimated for a molecule of known dipole moment. The method is based on the fact that σ_p is composed of two parts, one of which $\sigma_p(E)$ can only be obtained from a perturbation calculation. This latter 'high frequency' contribution can be made to disappear by an appropriate choice of origin, and Das and Ghose demonstrated that for the proton it is a very good approximation to take this origin as the electronic centroid. The remaining contribution, $\sigma_p(G)$ can be obtained from the ground state wave function and is proportional to the electric field at the proton, along the line joining the proton to the electronic centroid. They then make use of the fact that this field from the electrons must be equal and opposite to that provided by the nuclei. This enables one to determine $\sigma_p(G)$ without a knowledge of the ground state wave function.

Since the net field at the proton has been set equal to zero in the electrostatic density, the value of $\sigma_p(G)$ determined in this way is both the experimental and the predicted quantity. The only approximation is that of neglecting $\sigma_p(E)$. For water the formula becomes

$$\sigma_p(G) = -\frac{a^2}{3} \times R_c \times \left[\frac{1}{R_H^2} \cos\theta_H + \frac{\delta}{R^2} \cos\theta_0 \right]$$

R_c here refers to the distance in a.u. between the proton and the electronic centroid, which can be determined from the known dipole moment. The angles are measured relative to R_c from the proton. For water this contribution is calculated to be -7.76×10^{-5}. This can be compared to the calculated values (74) of -8.66 (experimental, $-7.98) \times 10^{-5}$ for hydrogen fluoride and -6.66 (experimental, $-6.76) \times 10^{-5}$ for ammonia. Therefore this estimate for water is undoubtedly an upper limit, which implies that the total shielding constant obtained by combining it with the calculated diamagnetic part is a lower limit. These values are

σ (electrostatic)	$\geq 2.85 \times 10^{-5}$
σ (Das and Ghose)	$\geq 1.89 \times 10^{-5}$
σ (Ellison and Shull)	$\geq 1.39 \times 10^{-5}$

The experimental value is 2.97×10^{-5} according to Das and Ghose, from measurements of Gutowsky and Hoffman (87) on the chemical shift of hydride molecules relative to methane. More recent values obtained by Schneider and coworkers (65) place this shielding constant at 3.02×10^{-5}. Both of these estimates are based on a value of 2.66×10^{-5} for the shielding constant of a proton in the hydrogen molecule.

The electrostatic density predicts the best value of this property and the agreement may well be improved with a good determination of σ_p. Both of the other densities predict values which are too low due to the orbital exponent of 1.00 for the h orbital, but an improvement over those estimated by Das and Ghose by combining their σ_d with a σ_p determined from a variation calculation.

IV. THE AMMONIA MOLECULE

The calculation of the forces exerted on the nuclei in the water molecule demonstrated that a methane-like distribution of density is extremely unstable electrostatically in that molecule as in hydrogen fluoride.[1] Several features of the predicted electrostatic density for water were reflected in the S.C.F. density - very little lone pair hybridization, and bonds primarily p in character but concentrated between the bond axes rather than along them. The use of an empirically determined orbital exponent for hydrogen was justified by the good estimates obtained of the proton shielding constant and the diamagnetic susceptibility. In ammonia there are again six parameters, since the introduction of an extra bond orbital does not result in any new orthogonality conditions. The directions of the three force components are shown in Figure 15 and are labelled F_N, $F_\perp$ and $F_\parallel$. The equivalent orbitals are set up under the same limitations assumed for the water molecule and the exponents are chosen in the same manner. It is found that the forces vary in a precisely analagous fashion, which leads to a distribution exhibiting the same

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[1] This confirmation of the validity of the general rule proposed in Part I regarding hybridization in hydride molecules with lone pairs of electrons is further substantiated by the following calculations for the ammonia molecule.

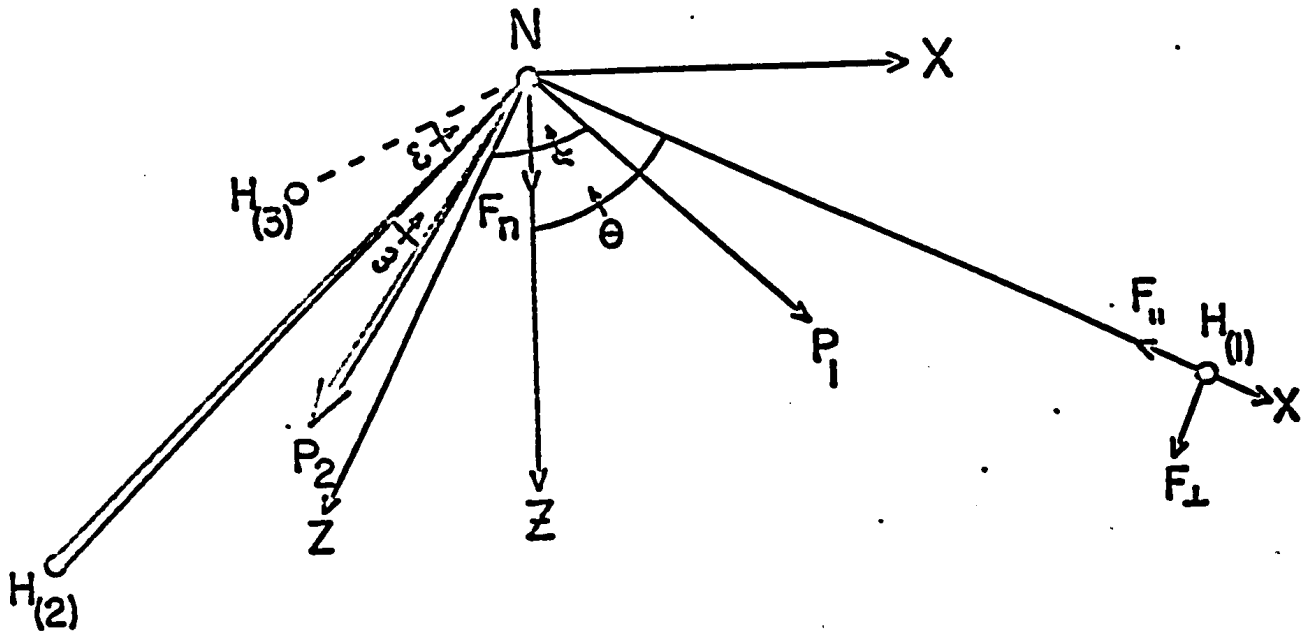

FIGURE 15. The co-ordinate system used in the calculation of the density in H_3. The arrows indicate the directions of the positive forces F_n, $F_\perp$ and $F_\parallel$. $H_{(2)}$ has a positive Y co-ordinate.

characteristics as above at electrostatic equilibrium. In the present case there are two good S.C.F. calculations (88,89) available which predict hybridizations intermediate between those of the electrostatic density and that obtained by the method of Duncan and Pople (43). This permits a correlation of the magnitude of the calculated properties with certain features of the distributions, which indicates the region of the density which is tested by each property. In addition, since both S.C.F. calculations used $\zeta_{(H)} = 1.00$, a comparison of the calculated properties confirms the importance of using a larger value of this exponent.

Method of calculation.

Slater atomic orbitals are employed for the basis functions. The nitrogen 1s, 2s and 2p orbitals are given the free atom orbital exponents of 6.70, 1.95 and 1.95 respectively. The hydrogen 1s orbitals are assigned an effective nuclear charge of 1.29 on the basis of the rule discussed in the case of water which relates the effective nuclear charge to the separated and united atom limits. The calculations are performed for a bond length of 1.905a.u. and a bond angle of 107.3° (78).

The single determinant wave function is expressed in terms of equivalent orbitals embodying the same five

parameters as those for water. These orbitals are

$$\psi_0 = 1s$$

$$\psi_1 = \cos\varepsilon_1 s - \sin\varepsilon_1 p_Z$$

$$\psi_{bi} = \lambda[\cos\varepsilon_b\, s + \sin\varepsilon_b\, p_i] + \mu[h_i - \delta(h_j + h_k)]$$

The p_i are 2p orbitals directed as shown in Figure 15 (note that they do not necessarily coincide with the bond axes) and p_Z is directed along the Z axis. The requirements of orthogonality, as expressed in the conditions that (i) $\int \psi_{bi}\psi_{bj}d\tau = 0$ and (ii) $\int \psi_{bi}\psi_1 d\tau = 0$ give rise to the following equations relating the orbital parameters:

$$\text{(i)}\quad \lambda^2[\cos^2\varepsilon_b + \sin^2\varepsilon_b \cos\omega] + 2\lambda\mu[\cos\varepsilon_b S_2(1-2\delta) + \sin\varepsilon_b(\mathcal{X} - \delta(\cos\omega + \mathcal{X}))\, S_3] + \mu^2[S_1 + \delta^2(1 + 3S_1) - 2\delta(1 + S_1)] = 0$$

where $\mathcal{X}$ is the component of p_3 and p_4 along the x axis,

$$\mathcal{X} = \cos(\theta-\omega)\cos\theta - (1/2)\sin(\theta-\omega)\sin\theta;$$

and

$$\text{(ii)}\quad \tan\varepsilon_1 = \frac{(\lambda/\mu)\cos\varepsilon_b + S_2(1-2\delta)}{\cos\theta S_3(1-2\delta) + (\lambda/\mu)\sin\varepsilon_b\cos(\theta-\omega)}$$

A third condition obtained from the normalization of the bond orbitals allows an evaluation of λ and of μ once their ratio has been chosen:

$$(iii)\ \mu^2 = 1/[(\lambda/\mu)^2 + 1 + 2\delta^2(1 + S_1) - 4\delta S_1$$

$$+ 2(\lambda/\mu)(\cos\varepsilon_b S_2(1-2\delta)$$

$$+ \sin\varepsilon_b S_3(\cos\omega - 2\delta\mathcal{K}))]$$

Since five parameters are involved in determining the density distribution it was necessary to program the calculations for machine computation. The sequence of steps is the same as for water and is outlined in a flow chart in the Appendix.

Since the orbitals are mutually orthogonal and doubly occupied the electron density is

$$\rho = 2(\psi_{b1}^2 + \psi_{b2}^2 + \psi_{b3}^2 + \psi_1^2 + \psi_o^2).$$

The conditions for electrostatic equilibrium are, when $F_\perp$ and $F_\parallel$ refer to the electronic forces exerted on $H_{(1)}$,

$$F_\perp = F_\perp(\psi_{b1}^2) + 2F_\perp(\psi_{b2}^2) + F_\perp(\psi_1^2) = (1/R_H^2)\sqrt{3}\cos\theta$$

$$F_\parallel = F_\parallel(\psi_{b1}^2) + 2F_\parallel(\psi_{b2}^2) + F_\parallel(\psi_1^2)$$

$$= (7/R^2) + (1/R_H^2)\sqrt{3}\sin\theta$$

$$F_N = 3F_N(\psi_b^2) + F_N(\psi_1^2) = (21\cos\theta/R^2)$$

When no distinction is made between the forces exerted by the ψ_{bi} in any of the force expressions, the forces are equal. Explicit expressions for the forces are given in the Appendix.

Application of electrostatic criteria.

Pople and Duncan (43) have determined a density distribution for the ammonia molecule using the same equivalent orbitals with $\delta = 0$ and $\alpha = \varepsilon$. This leaves only one parameter, λ/μ, to be determined once the orthogonality requirements are taken into account. The dipole moment was used to fix this parameter. Such a distribution is the simplest that one can construct for the ammonia molecule. It is of interest to see how close their distribution comes to predicting zero resultant forces.

Since α is set equal to ε in this case, the hybridization of the bond and lone pair orbitals is largely determined by the molecular geometry. The bond angle is close to the tetrahedral angle and this fact together with the orthogonality conditions results in approximately sp^2 hybridization for the lone pair orbital. The lone pair is very dominant in this distribution as it is projected out from the nitrogen nucleus along the

symmetry axis and contributes a large atomic dipole to the dipole moment of the molecule. Consequently a polarity factor λ/μ of less than unity (0.838) is required to balance the observed and calculated dipole moments.

The projection of the lone pair electron density away from the nitrogen nucleus results in a large imbalance in all of the forces exerted on the nuclei. Figure 16 shows the relative magnitudes of the orbital contributions to $F_\perp$ and $F_\parallel$. It is seen that the density in the lone pair orbital exerts a perpendicular force on the hydrogen atoms which is actually greater than and opposite in sign to the electronic forces due to the density in the bond orbitals. The net result is an electronic force $F_\perp$ = -0.004 a.u. which, rather than opposing the nuclear repulsion of -0.068 a.u., adds to it to give a large resultant force tending to open up the bond angle. In the same manner, as indicated in Figure 16, the projection of the lone pair electron density above the nitrogen nucleus results in a large force on this nucleus which is actually greater than the forces exerted in the opposite direction by the electron density in the bond orbitals. The result is again a net force of repulsion on the nitrogen nucleus actually greater than the force of the nuclear repulsions alone. Due to the ineffective

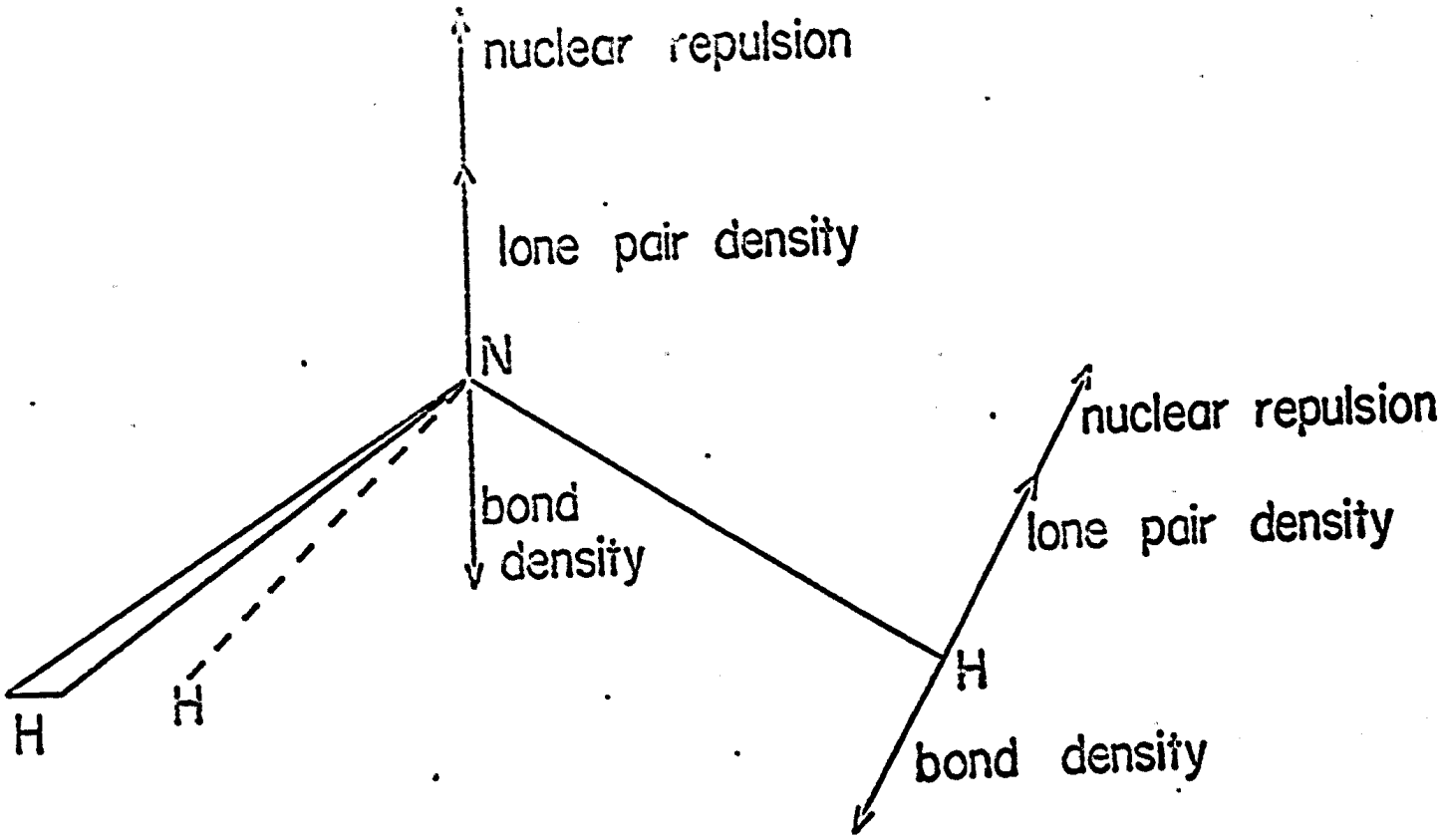

FIGURE 16. Orbital contributions to the force on nitrogen and on a proton perpendicular to the bond axis (not drawn to the same scale) for a density with a prominent lone pair of electrons in NH_3.

shielding provided by the lone pair electrons $F_{\|}$ is not large enough in magnitude to balance the nuclear repulsions exerted on the hydrogen nuclei along the bonds. This simple density distribution is far removed from a true equilibrium one.

If one relaxes the restraint that the bond orbitals point at the hydrogen nuclei then it is possible to decrease the p atomic orbital character of the lone pair electrons by bending the bonds ($\alpha \neq \varepsilon$). Discounting for the moment the effects of the overlap with the hydrogens, the lone pair orbital will be a pure s orbital (no p character) when the bond orbitals are pure p orbitals. When the lone pair electrons occupy an s orbital they do not exert a force on the nitrogen nucleus nor do they contribute to the perpendicular forces on the hydrogen nuclei. In this same limit the lone pair electrons exert a larger force on the hydrogen nuclei along the bonds as more density is placed between the N and H nuclei than when they are in a hybrid orbital. Taking into account the overlap with the hydrogen h orbitals, it is found that the orthogonality conditions force negative s character into the bond orbitals when this limiting form of an s orbital is approached for the lone pair. A calculation of the forces for a density distribution with bent bonds but no delocalization ($\delta = 0$)

does give results which are very superior to those obtained when $\alpha = \varepsilon$. F_s, $F_\perp$ and $F_\parallel$ are all increased as α is decreased and the lone pair orbital acquires an increasing amount of s character. However, as the increased s character of the lone pair orbital is attained only at the expense of introducing negative s character into the bonding orbitals, it is still not possible to obtain a density function which meets the requirement of zero resultant forces.

Final electrostatic equilibrium can be attained only by introducing the delocalization parameter δ. The reasons for this are not difficult to understand. By delocalizing the hydrogen orbitals the overlap between the hydrogen orbitals is substantially decreased. This decreased overlap allows for a greater degree of bending of the bonds (smaller α) as the bond orbitals may now approach more closely than before. In addition, the overlap of the hydrogen orbitals in each bond orbital with the s orbital is decreased by a factor of $(1-2\delta)$. Hence it is necessary to introduce only small amounts of negative s character into the bond orbitals to maintain the orthogonality as the orbital angle is decreased.

Characteristics of electrostatic density.

With the introduction of delocalization it is

possible to obtain very satisfactory distributions, close to electrostatic equilibrium. (It will be recalled that in the water molecule it was necessary to specify a narrow range of parameters and select the best average value.) In fact one can predict a value for the dipole moment in the present case, by finding that distribution which balances the forces on the proton and makes the force on the nitrogen nucleus a maximum. As always, these conditions are satisfied when there is no lone pair hybridization. Consequently the bond orbitals are primarily of p character and possess a high polarity of 1.5- too high in this case, since the predicted dipole moment of 0.67 a.u. is larger than the experimental value by 0.10 a.u. The orbital contributions to this density, labelled Case 1, are presented in Table X. The density labelled Case 2 is obtained by requiring that the dipole moment be correct. Both the dipole moment and $F_{\|}$ are very sensitive to the bond polarity; a value of 1.37 is required to reproduce the experimental dipole moment and this predicts an $F_{\|}$ slightly smaller than the appropriate nuclear repulsion.

In general the orbital contributions to the forces in Case 2 are very similar to those in Case 1. The final discrepancy left in the force on the nitrogen nucleus is the same order of magnitude as that found on the oxygen nucleus in the calculations on the water

TABLE X.

Orbital contributions to the forces in the ammonia molecule.

Case 1.

	$F_\perp$	$F_\parallel$	F_N
ψ_o^2	0.0000	0.551	0.000
ψ_1^2	0.0000	0.471	0.000
ψ_{b1}^2	0.1067	0.474	0.638
$\psi_{b2}^2=\psi_{b3}^2$	-0.0197	0.297	0.638
Total electronic force	+0.0673	2.090	1.914
Nuclear repulsion	-0.0676	-2.100	-2.127

Case 2.

	$F_\perp$	$F_\parallel$	F_N
ψ_o^2	0.0000	0.551	0.000
ψ_1^2	-0.0013	0.470	-0.035
ψ_{b1}^2	0.1052	0.452	0.639
$\psi_{b2}^2=\psi_{b3}^2$	-0.0183	0.292	0.639
Total electronic force	0.0673	2.057	1.882
Nuclear repulsion	-0.0676	-2.100	-2.127

the force on the heavy nucleus. A coefficient of ~0.04 can be estimated for the amount of 2p that would have to be mixed in the inner shell for the nitrogen nucleus to attain electrostatic equilibrium when the above orthogonality is taken into account. The lone pair electrons exert very little force on the nitrogen nucleus or on the proton perpendicular to the bond axis. The penetration force they exert on the proton along the bond, 0.47 a.u., is much larger than the corresponding force of 0.33 a.u. for two electrons in an sp^2 orbital. It can be seen from Table X that the electronic force on the proton stabilizing the bond angle ($F_\perp$) comes from the density in the bond orbital for that atom. When the bonds are not bent ($\alpha = \varepsilon$) this same contribution is zero as the density in each bond orbital is symmetrically placed with respect to the bond axis. Bending the bonds moves density off the bond axes and leads to large attractive forces on the hydrogen nuclei and on the nitrogen nucleus. The effect of bending the bonds can be seen in a density contour diagram.

Lines of constant density in the ammonia molecule are shown in Figure 17, for the Case 2 density predicting the correct dipole moment. The upper diagram represents a plane passing through the molecular symmetry

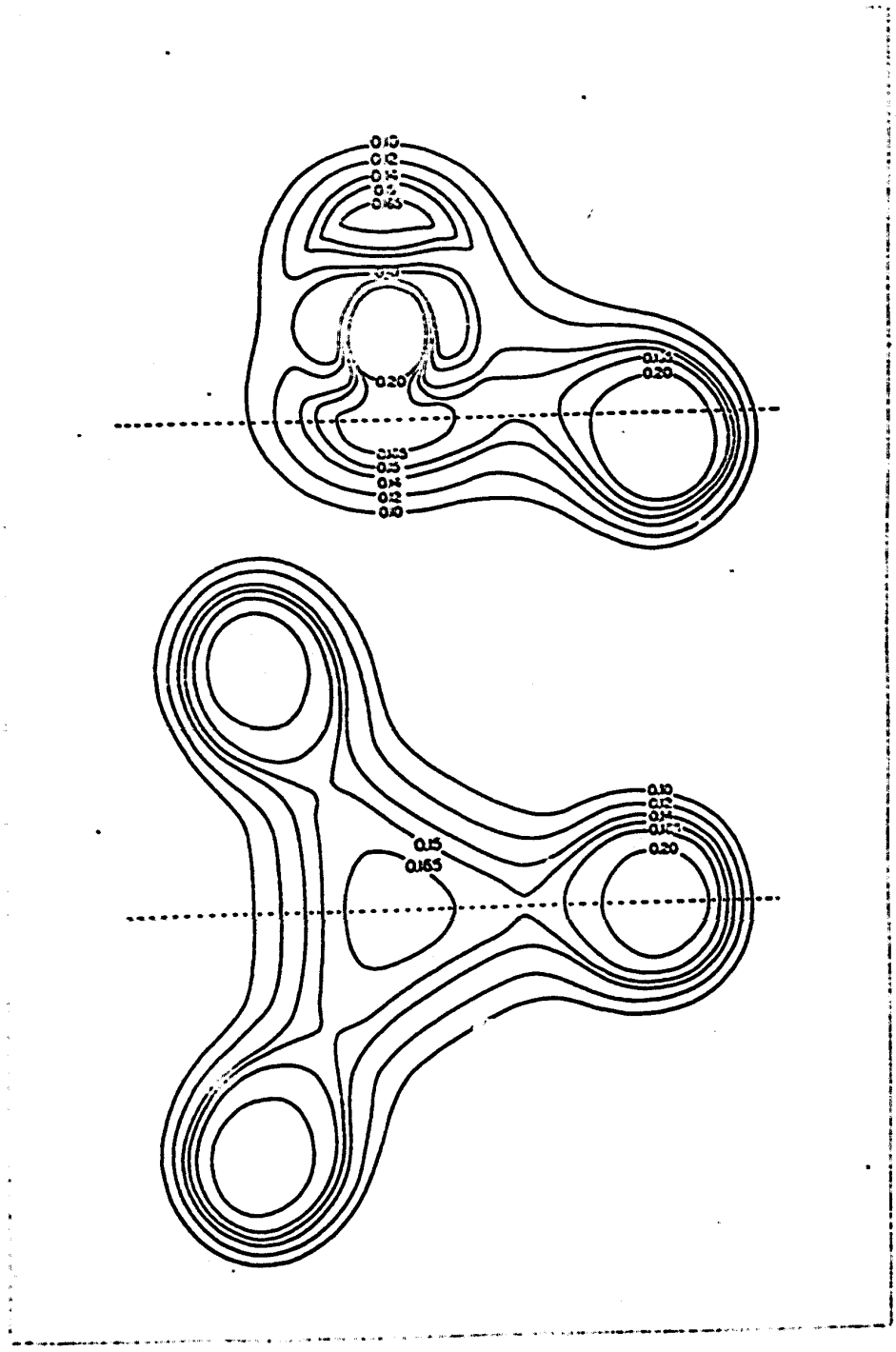

FIGURE 17. A density contour map in a.u. of the valence electrons of NH_3 in a plane passing through the symmetry axis and one of the protons. The section in the lower half of the diagram is a plane parallel to and slightly above the plane of the three hydrogen atoms.

axis and any one proton and the lower diagram is a plane parallel to and slightly above, the plane of the three protons. The similarity of the general features of the densities predicted by the electrostatic method for the ammonia and water molecules is reflected in the marked similarity of the respective contour diagrams (see Figure 14). The density in the N-H plane demonstrates the spherical nature of the charge distribution around the nitrogen nucleus, necessary to attain electrostatic equilibrium. As in the case of water, a distribution which predicts large s-p hybridization for the lone pair orbital shows a large deficiency in charge density below the nitrogen nucleus. This leads to an unbalanced force on the nitrogen nucleus, as is illustrated in Figure 16. Just as important, a removal of this density from below the nitrogen nucleus greatly reduces the binding of the protons. In the electrostatic distribution there is a large density concentration between all the nuclei, as shown in the lower diagram of Figure 17. It is so placed that it can attract all four nuclei simultaneously. A great reduction in this density such as that resulting from lone pair hybridization, is seen to be unjustifiable in terms of forces. It will be shown that it is also unfavourable energetically.

TABLE XI.

Comparison of parameters and properties of proposed electron density distributions for BH_3

	Electrostatic Case 1	Electrostatic Case 2	Kaplan S.C.F.(89)	Duncan S.C.F.(86)	Pople and Duncan(43)
type of orbital[1]	Slater	Slater	Hartree-Fock	Slater	Slater
hydrogen orbital exponent (ζ)	1.29	1.29	1.00	1.00	1.00
ε_1	0.006°	0.200°	32.5°	45.3°	52.1°
lone pair hybridization	s	s	$sp^{0.4}$	sp	$sp^{1.7}$
ε_b	96.47	98.80°	102.1°	72.1°	86.2°
ω	28.22°	28.56°	18.0°	10.5°	0°
α	68.00°	67.45°	83.1°	93.8°	106.8°
δ	0.3250	0.2800	0.206	0.157	0.000
λ/μ	1.510	1.374	1.368	1.228	0.838
	Electronic forces (nuclear repulsions[2] are -0.068 for $F_\perp$, -2.10 for $F_\parallel$ and -2.13 for F_N).				
$F_\perp$	0.068	0.068	-	0.026	-0.004
$F_\parallel$	2.09	2.05	-	2.00	1.81
F_N	1.91	1.88	-	0.08	-0.28

Table XI (cont'd.)

Dipole moment					
	(in a.u.; exp. = 0.574 a.u.)				
D_l	0.000	0.010	-	1.494	1.446
D_b	-1.435	-1.538	-	-2.860	-3.029
proton moment	2.100	2.100	-	2.157	2.157
D	0.67	0.57	0.72	0.77	0.57
Nuclear quadrupole moment					
	(in units of 10^{-26} cm.^{2})[3]				
q_l	0.000	0.000	-1.365	-2.021	-2.436
q_b	-1.889	-1.824	-0.245	+0.627	+1.326
q_o	-1.889	-1.824	-1.610	-1.394	-1.090
Q	0.82	0.85	0.94	1.07	1.32
Diamagnetic susceptibility					
	(in units of 10^{-6} c.m.u./mole; exp.[4] = 20.6±0.8)				
χ_d	-18.6	-19.0	-	-20.9	-24.4
Proton shielding constant					
	($\times 10^5$; exp.[5] = 3.06×10^{-5})				
σ	2.84	2.87	-	2.54	2.47

1. In references 43, 88 and 89 $\epsilon = 106^{\circ}47'$ and $R = 1.916$ a.u. while the electrostatic calculations are based on the values $\epsilon = 107.3^{\circ}$ and $R = 1.905$ a.u. obtained by H.T. Weiss and H.W.P. Strandberg, Phys. Rev., 83, 567 (1951), and quoted in L. Sutton, Interatomic Distances. This gives rise to slight differences in the nuclear moments.

2. In references 43, 88 and 89 the nuclear repulsion for $F_{\parallel} = -2.08$ but the other two repulsions are the same to the significant figures quoted.

3. The experimental coupling constant $eQq = -4.0842$ Mc, measured by G.R. Gunther-Mohr, R.L. White, A.L. Schawlow, Phys. Rev. 94 1184 (1954). If the electric field gradient q is expressed in atomic units, $Q = [0.4256 \times 10^{-26}\ (eQq\ Mcs)/q]cm^2$. The nuclear contribution to q is taken as -0.2313, a value calculated by Kato(91)as an average over inversion doubling.

4. The experimental χ_d is found by combining the measured susceptibility of NH_3 vapour, $-16.3 \pm 0.8 \times 10^{-6}$ c.g.s.u./mole, from the work of C. Barter, R.G. Meisenheimer and D.P. Stevenson, J. Phys. Chem. 64, 1312 (1960) with the paramagnetic contribution of 4.3×10^{-6} c.g.s.u./mole which was calculated by Weltner (76) using the data of J.R. Eshbach and H.W.P. Strandberg, Phys. Rev. 85, 24 (1952). The calculated χ_d is referred to the centre of mass as origin.

5. The paramagnetic contribution is -6.78×10^{-5}, from the results of G.R. Gunther-Mohr, R.L. White, A.L. Schawlow, Phys. Rev. 94, 1184 (1954).

A comparison of different density distributions.

Table XI gives the parameters and properties for the density distributions obtained by the present electrostatic method, by S.C.F. calculations (88,89) and by Duncan and Pople (43). Of the two S.C.F. distributions given in Table II that obtained by Kaplan (89) must be judged the best as it gives a greater percentage of the total energy than does Duncan's (88) and in addition gives a better dipole moment. This is to be expected as Kaplan used Hartree-Fock orbitals for the nitrogen atom while Duncan employed Slater orbitals. To facilitate comparisons, the symmetry orbitals used by Kaplan were transformed into the same equivalent orbital representation employed to describe the other density distributions. The distribution obtained by Pople and Duncan (43) using the same basis set of atomic orbitals as Duncan, can be regarded as the simplest possible distribution which fulfills the orthogonality and dipole moment requirements.

It is interesting to compare the predicted densities in terms of the equivalent orbital parameters. Reference to Table XI indicates that the two density distributions obtained by the electrostatic method differ little in their essential features. The most striking feature of Table XI is the manner in which the predicted s-p hybridization of the

lone pair orbital decreases as the accuracy of the energy calculation increases. Both densities obtained by the electrostatic method place the lone pair electrons in what is essentially an s orbital. Kaplan's result of only 29% p character is in closer agreement with the electrostatic prediction of zero percent than are the 50% and 60% found by the other authors.[1] Also, in all other respects, the distributions obtained by the electrostatic method agree best with that found by Kaplan. Both electrostatic densities predict almost pure p bonds with a small amount of negative s character, as does Kaplan's. The bond polarities (λ/μ) are fairly large in these same three cases, to counterbalance the decreasing lone pair contribution to the dipole moment. The electrostatic densities predict the largest degree of bond bending and delocalization, the next highest values for both ω and δ being given by Kaplan's distribution.

i) Forces.

The forces predicted by the distributions obtained by Duncan and Pople and by Duncan are given in Table XI and it is evident that both distributions predict large resultant forces on the nitrogen and hydrogen nuclei.

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1. The use of the free atom exponent for hydrogen in the energy calculations would restrict the amount of bond bending and hence the limit of lone pair hybridization, since the h-h overlap is 0.33 compared to 0.19 in the electrostatic calculations.

The principal reason for these great imbalances between the nuclear and electronic forces is due to the large amount of s-p hybridization in the lone pair orbital. The forces have not been calculated for Kaplan's results because of his use of Hartree-Fock orbitals for the nitrogen atom. However, the Hartree-Fock orbitals are very similar to the orthogonalized Slater forms for the 1s and 2s orbitals and differ primarily in the 2p functions. For this reason one can be certain that while Kaplan's results will predict smaller resultant forces than those of Duncan (his parameters are close to those obtained by the electrostatic methods) they will not be zero. An sp hybridization of 29% p character in the lone pair orbital corresponds to an asymmetric distribution of the charge density around the nitrogen nucleus that is not compensated for by other factors in the distribution. Thus while these S.C.F. calculations give an upper bound to the energy they do not necessarily give densities for the ammonia molecule which are acceptable in terms of the forces which they predict. This was found to be the case for the water and hydrogen fluoride molecules as well.

(ii) Dipole Moment

Of the three distributions reported in Table XI which did not employ the dipole moment to fix a parameter,

the Case I electrostatic density is in closest agreement with experiment. The electrostatic density predicts a dipole moment which is too large by 0.23 Debyes, while the distributions obtained by the variational methods predict values that are too large by 0.37 and 0.50 Debyes,[1] Kaplan's result being the better of the two.

It has frequently been suggested that the major electronic contribution to the dipole moment of the water and ammonia molecules is from the atomic dipole created by the s-p hybridization of the lone pair electrons. Indeed, it is suggested that only through large atomic dipoles can these moments be explained. This conclusion is arrived at only if one assumes that the hybridization must be determined by the molecular geometry. Actually, one finds that it is possible, through the mechanism of bent bonds, to match the observed dipole moments of the ammonia and the water molecules for the complete range of allowed hybridizations on the nitrogen and oxygen atoms. Two factors are dominant in determining the dipole moment, namely the hybridization and bond polarity. Fixing the hybridization by requiring it to fit the molecular geometry

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1. Duncan (66) reported a dipole moment in very close agreement with the experimental value. On checking his calculations an error was discovered in the integral he labels $h_z z h_z$. The value should be 0.23976. The author agrees with the value now reported for his distribution. (Private communication).

forces the bond polarity to be H(δ^+) - H(δ^-) to partially balance the large atomic dipole created by the ammonium lone pair. This occurs in the dipole contributions to Bonle's density in Table XI. Allowing for bent bonds reduces the lone pair contribution and restores the more conventional sense to the bond polarity, H(δ^-) - H(δ^+). At least part of the error in the overestimation of the dipole moment in the variational calculation must be due to the remaining hybridization predicted for the lone pair orbital.

(iii) Quadrupole Moment.

The quadrupole moment Q of the N^{14} nucleus has not been measured. Therefore, it is not possible to experimentally determine the electric field gradient q at the nitrogen nucleus from the measured N^{14} coupling constant for the ammonia molecule using the relationship, coupling constant = eq Q. However, one can calculate the electric field gradient for the electrostatic and S.C.F. density distributions and use these to predict values for Q. These values may be compared and any trend in the Q values with known accuracy of the wave functions can be noted.

The electronic contribution to the electric field gradient q_e along the symmetry axis of the ammonia molecule is largely determined by the amount of 2p character on the

symmetry axis (z axis) relative to the amount at right angles to this axis, since the spherical distributions make no contribution and there is a small, almost constant contribution of about 0.35. The contribution from a p_z orbital is a factor of (-2) times that for a p_x or p_y orbital. Considering only the contributions from the p orbitals Townes and Dailey (90) state that the bonds in the ammonia molecule cannot be largely p in character (as predicted by the electrostatic densities) as the observed coupling constant for the ammonia molecule would then be small or zero. The qualitative basis for this argument is easy to understand. It is again based on the incorrect assumption that bonds largely p in character must correspond to orbital angles of 90° or greater. In this limit the lone pair is in an s orbital and gives no contribution to q_e and the contribution for the parallel and perpendicular components of the p orbitals will largely cancel for $\alpha > 90^\circ$. Thus they conclude that the bonds and the lone pair must be s-p hybrids in order to account for a relatively large value of q. Their approach is exemplified by the values obtained for the Pople distribution. Here (see Table XI) a large contribution to q_e is obtained from the lone pair density which more than offsets the positive contribution from the bonding orbital.

It would seem that any loss of s-p hybridization of the lone pair orbital must lead to a decrease in the absolute value of q_e. However, in actual fact to reach the limiting s form for the lone pair one must bend the bonds to orbital angles of less than 90°. On doing this, the contribution to q_e from the bond orbitals (which are now almost pure p) actually becomes negative since now a larger component of the p orbitals is placed along the z-axis than perpendicular to it. In fact, the contributions to q_e from Kaplan's density distribution or from the electrostatic distributions are seen to predict even larger values for q_e than did Pople's even though the lone pair contribution is much reduced or zero. Therefore, it is not necessary to postulate significant amounts of s-p hybridization to account for the observed nuclear coupling constant or the dipole moment of the ammonia molecule. The Q values quoted in Table XI for the density distributions other than the electrostatic ones have been calculated by Kato (91). The values for the distributions of Kaplan and Duncan have been recalculated in the equivalent orbital form and agreement was found with the final values reported by Kato. As the accuracy of the wave function is increased, the absolute value of q is seen to increase (from 1.09 for the Pople density to 1.61 for Kaplan's) and consequently the predicted values for Q decrease.

The electrostatic evaluations of Q are in best agreement with the value predicted by Kaplan's distribution. Since Kaplan employed Hartree-Fock orbitals for the nitrogen atom his value for Q should be more reliable than that determined from Duncan's distribution. The downward trend in the value of Q would suggest that the value for N^{14} is around 0.9×10^{-26} cm^2 or less, rather than the value of 2×10^{-26} cm^2 commonly quoted (92). This was the value suggested by Townes and Dailey (90) as that which would best fit the observed quadrupole coupling constants of a range of nitrogen-containing substances. However, their choice was based on qualitative considerations of hybridization in these compounds and is therefore subject to errors such as was discussed for ammonia.

(iv) Diamagnetic susceptibility.

The diamagnetic susceptibility is determined largely by the density in the outer regions of the molecule. Its value is quite independent of the hybridization of the nitrogen atom since the s and p orbitals make approximately equal contributions to χ_d, as do their overlaps with the hydrogen orbitals. However, bond polarity and the orbital exponent for the hydrogen h orbitals do play a dominant role in determining χ_d. These parameters control the amount of density on the hydrogen nuclei, which are the centres of charge most distant from the origin. A small λ/μ ratio weights the hydrogens and thus increases the absolute magnitude of χ_d. A low value of the hydrogen orbital exponent results in a more diffuse density in the outer regions of the molecule and this also leads to an increase in the absolute magnitude of χ_d. From these considerations one would expect the densities determined by Pople and Duncan and by Duncan to give larger values for $|\chi_d|$ than those determined from the electrostatic densities. This is the case as noted in the results for χ_d given in Table XI. The densities determined by Pople and Duncan have a high susceptibility due to the relatively low values of λ/μ and the orbital exponent for the hydrogen orbitals. The values given by the electrostatic densities correspond to a more contracted density distribution and

are in agreement with the value of -18.70 (in the units used in Table XI) obtained by Banyard (85) from a central field wave function for the ammonia molecule. The density obtained by Banyard satisfactorily accounts for the over-all radial distribution in the ammonia molecule as determined by X-ray scattering measurements.

As in the case of the water molecule, the experimental value is bracketed on one side by the electrostatic and central field densities and on the other by the S.C.F. density. This indicates that the charge densities obtained by the electrostatic and central field methods are too contracted around the proton, while that obtained from the S.C.F. calculation is rather too diffuse.

(v) Proton magnetic shielding constant.

The experimental proton shielding constant of ammonia vapour differs from that of water vapour by the observed chemical shift, 0.65 p.p.m.(65). This yields $\sigma = 3.04 \times 10^{-5}$ or 3.08×10^{-5}, depending on the value chosen for water. An average value is quoted in Table XI. Once again the density immediately surrounding the proton is of primary importance in determining the shielding. The more diffuse, i.e., the smaller the orbital exponent of the hydrogen h orbital, the smaller will be the predicted value of $\langle 1/r_H \rangle$. Large values of λ/μ will also decrease

$\langle 1/r_p \rangle$ by shifting density away from the proton. These trends oppose each other in the densities listed in Table XI, since those densities which have $\zeta = 1.00$ have smaller values for λ/μ than do the electrostatic densities with $\zeta = 1.29$. In the determination of χ_d both trends operated in the same direction. As can be seen from the results, however, the effective nuclear charge is the all-important factor. Both densities which use $\zeta = 1.00$ predict $\sigma = 2.5 \times 10^{-5}$, in spite of their different overall distributions, while the electrostatic densities with $\zeta = 1.29$ give $\sigma = 2.9 \times 10^{-5}$. Although the electrostatic densities have yielded a value for σ_d in close agreement with experiment, it must be pointed out that this is in reality not a good overall test of a density function. The value obtained for σ_d depends so much on the value chosen for the single parameter ζ, that it is possible to obtain as good an estimate for σ_d by using a Pople-like distribution with a $\zeta = 1.29$. Changing the orbital exponent in Duncan and Pople's approach does not affect the basic characteristics of the density predicted. Thus two distributions which differ radically in every way except in that they have the same value for ζ, give almost the same answer for σ_d. However, the results do emphasize the importance of allowing for an effective nuclear charge

for hydrogen greater than unity. In fact, the proton shielding constant is probably the most sensitive criterion available for testing one's choice of hydrogen screening constant. On this basis the empirical rule used here to calculate the orbital exponent of 1.29 gives a good estimate of the magnitude of ζ for a proton in the ammonia molecule.

V. COMPARISON OF BOND PROPERTIES

Realization of the effect of prominent lone pairs of electrons on the dipole moment has cast doubt on the validity of a correlation of this moment with bond properties such as bond moments, ionic character and electronegativity differences between the constituent atoms (21). Since such qualitative concepts have proved very valuable in the co-ordination of many chemical phenomena and in the prediction of properties (one well-known example is Pauling's prediction of a dipole moment of 1.8 D. for hydrogen fluoride on the basis of electronegativity before it was measured to be 1.820 Debyes), it is highly satisfactory that the present results confirm the important role played by bond electrons rather than lone pair electrons. Having obtained density distributions for hydrogen fluoride, water and ammonia it is of interest to compare them as a series, noting those characteristics which are common and those which are unique to a particular bond. Correlations between the predicted bond properties and those obtained by qualitative reasoning or inferred from experimental observations can be examined.

The fact that the bonds are strongly bent in ammonia and in water does not prevent one from ascribing a bond moment to each equivalent bond orbital, of magnitude 1.32, 1.51 and 1.82 Debyes in the series N-H, O-H and F-H.

these moments show a close correlation to the predicted polarity ratios of 1.37, 1.51 and 1.69 in these bonds. It is of interest to compare these quantities with the electronegativity differences between the component atoms. Pritchard and Skinner (93) have discussed the different scales of electronegativity in great detail and their 'best' values are chosen for the present comparison. With these electronegativities of 2.1, 3.0, 3.5 and 3.9 for hydrogen, nitrogen, oxygen and fluorine the differences in the hydrides are 0.9, 1.4 and 1.8. The agreement between all three scales in water and hydrogen fluoride is perhaps fortuitious, as there is no correlation in the case of ammonia. But the trend in the polarities is that predicted by the electronegativity values.

The large electronegativity difference between the nitrogen and fluorine atoms has led to the belief that the small observed bond moment of 0.16 D. in nitrogen trifluoride can only be explained by a large contribution from a prominent lone pair of electrons on the nitrogen atom (21). In ammonia the bonds are considered to be less polar (it will be recalled that in the tetrahedral description of the density the bond orbital actually has a $\lambda/4$ of less than unity) and therefore do not provide a moment large enough to counteract the lone pair atomic dipole. This reasoning has been widely quoted as evidence for the importance of

the lone pair contribution to the dipole moment in ammonia and nitrogen trifluoride. However, it has been shown that the observed dipole moment in ammonia can be reproduced without lone pair participation when the bonds are allowed to bend. Just as the electronegativity difference in an N-H bond is not a good measure of the bond moment or polarity, it might not be a reliable criterion in the N-F bond either. Thus the dipole moment of nitrogen trifluoride can be explained by other distributions as well as that with large lone pair contributions.

One very sensitive criterion of the small variations in the electron density distributions found in isoelectronic or homologous sequences is the magnetic shielding constant. The proton magnetic shielding constant might be expected to be particularly sensitive to changes in the immediate environment. For most series the shielding constant varies in a regular fashion which can be explained on the basis of electronegativity. One such example is the chemical shift of a methyl proton in substituted ethanes, which varies linearly with electronegativity of the substituent (93). However, for the first row hydrides the chemical shifts in the gaseous phase relative to methane are anomalously small (65)[1] and cannot be

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1. In the liquid phase the signals are shifted to much lower fields, indicative of the importance of hydrogen bonding in these molecules (65, 87).

explained solely on the basis of electronegativity. The graphs shown in Figure 18 shed some light on this problem. They give the concentration of density along an H-X bond as found by the electrostatic method. The height of the peak at the proton is very sensitive to the choice of orbital exponent for the hydrogen orbital. As discussed earlier, it is fairly certain that the empirical rule used to estimate this quantity rather overestimates it, which makes the water and ammonia peaks somewhat too high in Figure 18. One can therefore conclude that the concentration of density at the proton is very similar in the three molecules and furthermore, is very close to that of an isolated hydrogen atom (see Figure 11). The removal of density due to the increasing electronegativity of the heavy nucleus from NH_3 to HF appears to be compensated for by a more efficient concentration of the remaining density, as shown by the increasing orbital exponents. Hence in this particular series of molecules, there is obviously no simple relationship between the electronegativity and the shielding constant. If one takes a series such as the substituted ethanes, the C-H bond length will be relatively unaffected by the fairly distant substitution of electronegative groups and hence the orbital exponent (as determined by the empirical rule) will remain constant. As a result there is a good

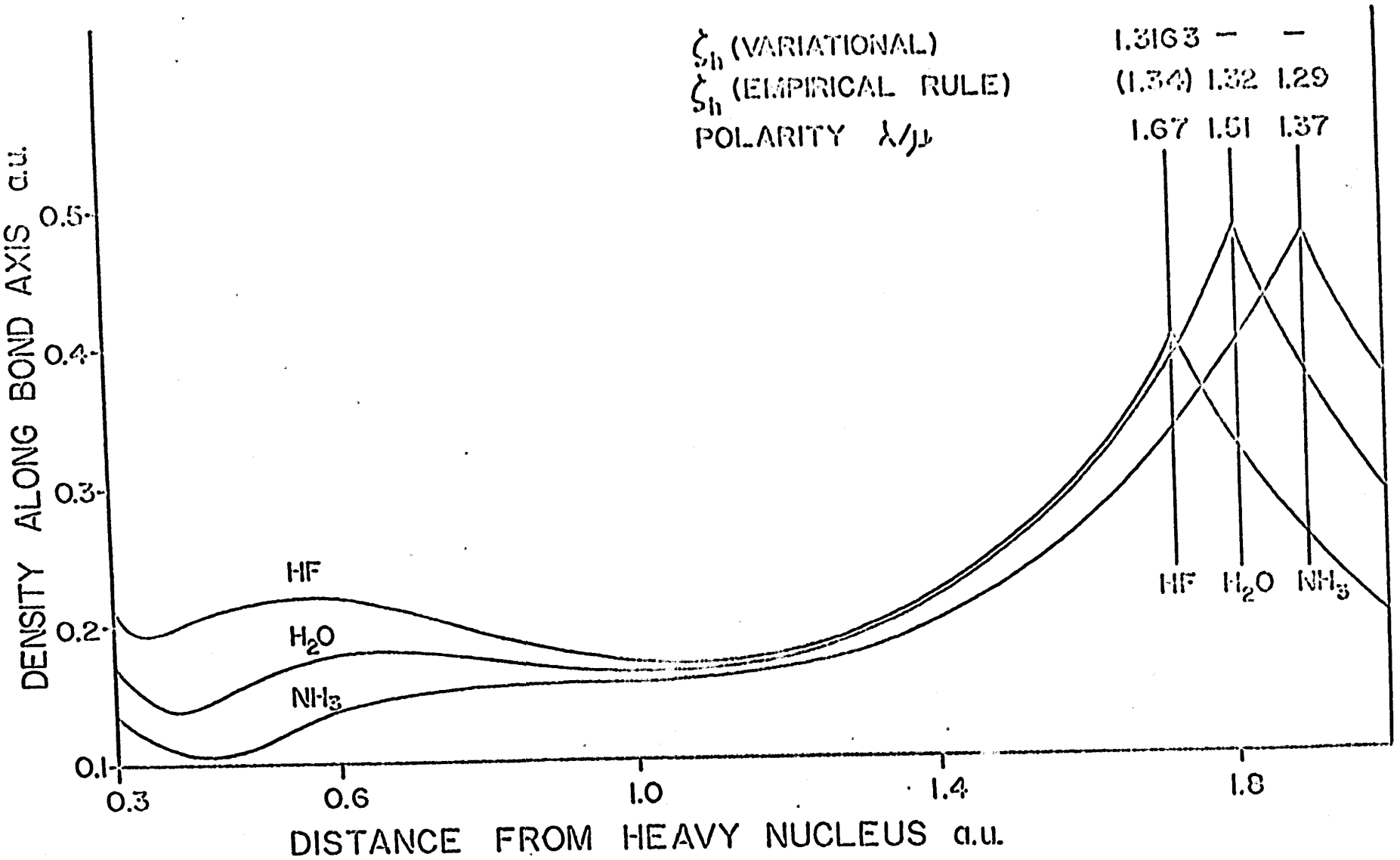


FIGURE 18. A comparison of the density along the N-H, O-H and F-H bond axes.

correlation between electronegativity and shielding constant.

The order predicted for the chemical shift from the electrostatic densities is HF>NH_3>H_2O. The total variation is only 1p.p.m. which is the same order as the absolute error of the predicted values. Obviously it would be desirable to have all the exponents determined by optimization in order to make a dependable estimate of the relative chemical shifts in this series. In other series which have much larger variations in shielding constant and smaller changes in orbital exponent, this is likely to be less important. Experimentally, the shielding constant of NH_3 is 0.65p.p.m. larger than that of H_2O and if HF really does coincide with CH_4 as suggested earlier, it would lie 0.05p.p.m. below NH_3.

Another sensitive probe of the detailed electron distribution in a bond is provided by the quadrupole coupling between a nucleus and its electronic environment. As pointed out in the discussion of the properties of ammonia, the conclusions drawn by Townes and Dailey (90) about the relationship of the quadrupole coupling constant in ammonia to the hybridization present were invalidated by their correlation of molecular geometry with hybridization. The same is not true of hydrogen fluoride, however, so it is of interest to examine the predictions of hybridization in

the hydrogen halides on the basis of quadrupole coupling data. From a consideration of observed quadrupole coupling constants for chlorine compounds and heavier halogens, Townes and Dailey have proposed the rule (95) that "the halogen bonds are hybridized with 15% of s character whenever the halogen is more electronegative by 0.25 units than the atom to which it is bonded". Gordy (96) attributed all of the observed coupling to the ionic character of the bond and disregarded hybridization. In the electrostatic density for hydrogen fluoride the amount of s character in the bond orbital is 15%; but while the sp hybridization of Townes and Dailey was thought to occur between the nuclei the present results indicate that it is in the opposite sense, since the coefficient of s is negative. It might be regarded as 'forced' hybridization (in Mulliken's terminology) since it is necessary to maintain orthogonality between the lone pair orbital and the bond orbital.

One bond property of considerable chemical interest is the bond strength. The average bond energy increases from ammonia to hydrogen fluoride and the bond length decreases, indicative of the increasing bond strength. Figure 18 shows that the density along the internuclear axis does increase slightly. However, it

is by no means obvious that this leads to a stronger bond, since so much density has been moved off the bond axis in ammonia and in water. Now the forces operating in these bonds depend upon the overall density distribution, and should provide a sensitive indication of the bond strength. A force analysis of the electrostatic density distributions similar to that used to examine the density in hydrogen fluoride can be performed. The force component which is most indicative of the strength of the bond is that on the proton along a bond axis, which is therefore examined in detail. In the assignment of nuclear repulsions to individual orbitals in the polyatomic molecules, the lone pair electrons and inner shell electrons are considered relative to the same number of nuclear charges. The remaining nuclear force then has to be balanced by that of all of the electrons in the bond orbitals. Those densities are chosen for the three molecules which have the correct dipole moment. Consequently the net force on the proton in ammonia and water is not quite zero in the force analyses given in Table XII.

In water and ammonia the sigma lone pair orbital ψ_1 is not antibinding because 2s electrons shield only ~ 95% of their nuclear charge. The favourable direction of the lone pair hybridization in hydrogen fluoride overcomes this and actually predicts a slightly binding force for

TABLE XII.

Orbital contributions to the force along the bond axis on $H_{(1)}$ in NH_3, H_2O and HF.

NH_3:[1]	Overlap force	Penetration force	Electronic force	Nuclear force	Force on $H_{(1)}$
ψ_o	.000	.551	.551	-.551	.000
ψ_1	.000	.471	.471	-.551	-.081
ψ_{b1}	.203	.249	.452	-.998	+.036
ψ_{b2}	.004	.288	.292		
ψ_{b3}	.004	.286	.292		
Total:	.211	1.847	2.058	-2.100	-.045
H_2O:[2]					
ψ_o	.000	.610	.610	-.610	.000
ψ_1	.000	.543	.543	-.610	-.067
ψ_π	.000	.456	.456	-.610	-.154
ψ_{b1}	.247	.326	.573	-.707	.195
ψ_{b2}	-.024	.353	.329		
Total:	.223	2.288	2.511	-2.537	-.026

1. The Case 2 density with the correct dipole moment.

2. The density at $\delta = 0.5$ with the correct dipole moment.

TABLE XII -(cont'd.)

HF[3]	Overlap force	Penetration force	Electronic force	Nuclear force	Force on $H_{(1)}$
ψ_o	.000	.672	.672	-.666	.006
ψ_1	.000	.701	.701	-.666	.035
ψ_π	.000	.511	.511	-.666	-.155
$\psi_{\bar{\pi}}$	.000	.511	.511	-.666	-.155
ψ_b	.232	.366	.598	-.333	.265
Total:	.232	2.761	2.993	-2.997	-.004

3. The density at $\varepsilon_1 = -6^o$ with the correct dipole moment.

this orbital, leading to a net zero force on the proton. The contributions of particular interest here are those from the bond orbitals. The net force per bond orbital increases markedly from 0.01 in ammonia to 0.10 in water to 0.26 in hydrogen fluoride, in a satisfactory parallel to the bond energies.

The increasing binding power of the bond electrons has to overcome the net antibinding force contributed to the molecules on successive replacement of bond orbitals by π lone pair orbitals. Each such pair of electrons

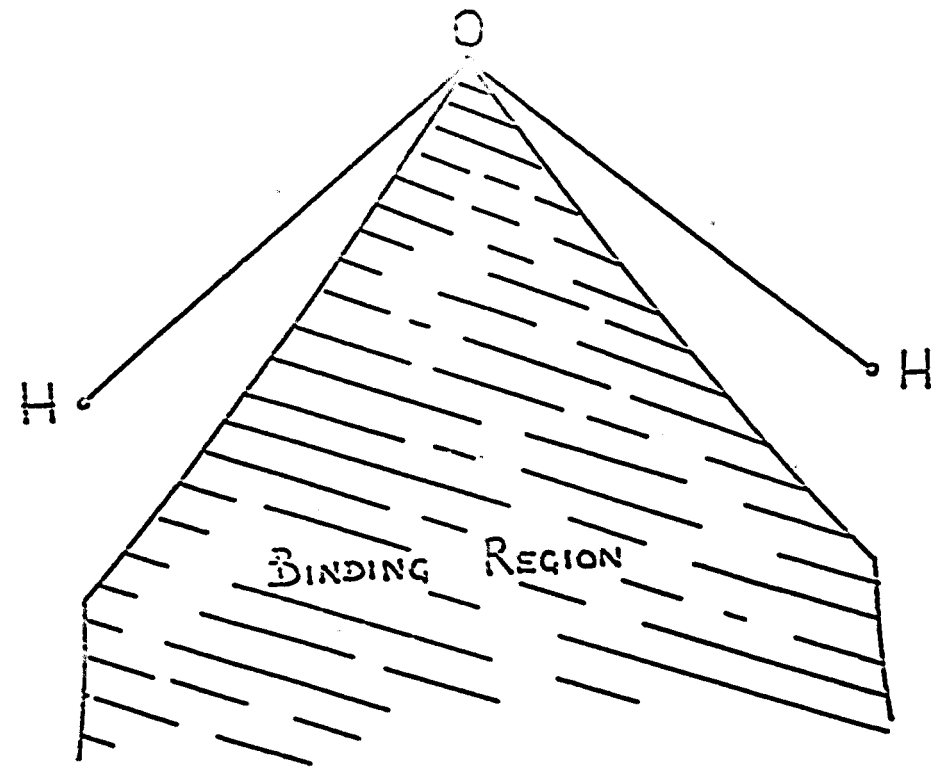
exerts a net antibinding force of -0.15 a.u. which has to be compensated for by the increased binding force of the bond electrons. This extra force comes from a more efficient shielding of the heavy nucleus, as measured by the penetration type forces, rather than from an increase in the overlap force. The amount of the total electronic force which arises from the overlap density remains fairly constant at ~9% throughout the series (the differences of 1% or 2% are not significant in view of the discrepancy in the total net forces). It appears that the increasing electronegativity of the heavy nucleus from ammonia to hydrogen fluoride concentrates charge around the nucleus so effectively that the bond length decreases and the bond strength increases in spite of the advers force exerted by the π electrons. This is in contrast to the homonuclear molecules, where no electronegativity effects can influence the binding. Consequently, the presence of the π lone pairs in the fluorine molecule results in an exceedingly weak bond, as discussed in Part I.

VI. CONCLUSION

Density distributions have been obtained for hydrogen fluoride, water and ammonia, by requiring that the net force on each nucleus in these molecules be zero. It has been demonstrated that in each case there could be no appreciable lone pair hybridization if the equilibrium configuration of the nuclei was to achieve electrostatic equilibrium. The determining principle governing the electronic distribution in the molecules may be summed up by the Berlin diagrams shown in Figure 19. It is apparent that these binding regions define the predicted positions of maximum probability of the overlap density.

In hydrogen fluoride (see Figure 11) the slightly asymmetric lean of the density above and below the fluorine nucleus towards the proton leads to an accumulation of charge in the binding region near the fluorine nucleus. Similarly the 'hole' behind the fluorine nucleus actually helps the binding since charge placed there would be strongly antibinding.

There is a binding zone for every pair of nuclei in a molecule. In the water molecule there are three such zones, which all contain the region shown in Figure 19. This region is one within which a negative charge will simultaneously



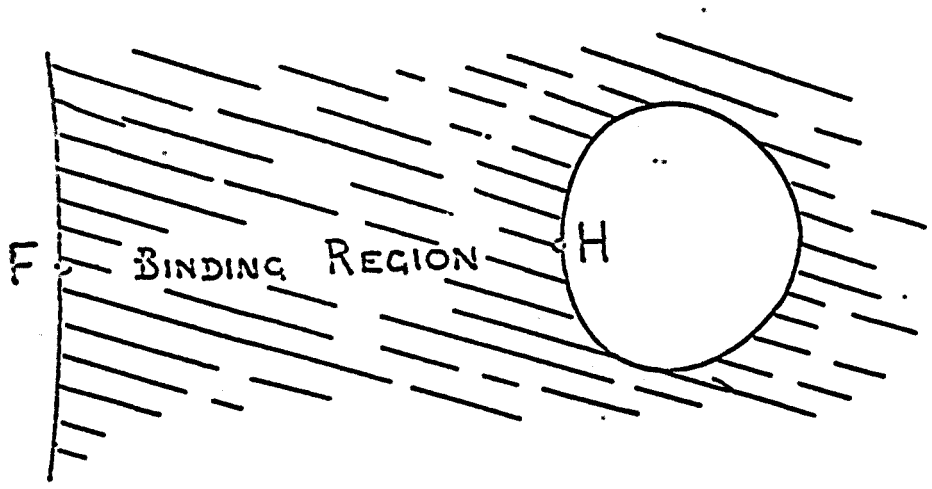


FIGURE 19. The binding regions in the molecules of water and of hydrogen fluoride.

bind all the nuclei. Along a bond axis a negative charge will bind one proton to the oxygen nucleus but will be in the antibinding region for the second proton and the oxygen nucleus. A comparison with Figure 14 illustrates that the electrostatic density predicts a concentration of charge in the Berlin binding region. The distribution of Duncan and Pople has virtually no density in this binding region. Part of it is in the weakly antibinding region along the bonds but the rest is above the oxygen nucleus where it is antibinding with respect to every combination of nuclei.

The binding region of ammonia (not shown) is analagous to that of water in three dimensions. Since the ratio Z_d/Z_p is fairly constant in the series FH - OH - NH, the binding regions for these pairs of nuclei are very similar to that shown for hydrogen fluoride. In ammonia the overall binding region therefore lies within the tetrahedron defined by the planes normal to each N-H bond through the nitrogen atom. Again this corresponds to the distribution in Figure 17 obtained by application of the electrostatic criterion.

In polyatomic hydride molecules with bond angles close to 90° it is apparent that far less delocalization and bond bending will be required to move density into the binding region. Perhaps the

first row hydrides of water and ammonia are anomalous in this respect (as in many others) on account of the very tight bonds. The repulsive force on a proton in hydrogen sulphide perpendicular to a bond is -0.050 a.u. at the bond angle of 93.3°, which is smaller than the repulsive force of -0.074 a.u. in water at 107.3°, due to the shorter bond length in water.

Thus the quantitative application of the Hellmann-Feynman theorem attempted in the present work has permitted an elucidation of the electronic structure of the molecules of ammonia, water and hydrogen fluoride, and of how this structure affects their properties. An attempt to understand the reason behind the calculated distributions leads one right back to Berlin's ideas of antibinding and binding regions. Since these regions have a physical significance (as well as an obvious pictorial appeal) in the molecules investigated here, it seems likely that this will prove true in other molecules as well. Such an approach to molecular geometry raises intriguing possibilities.

APPENDIX.

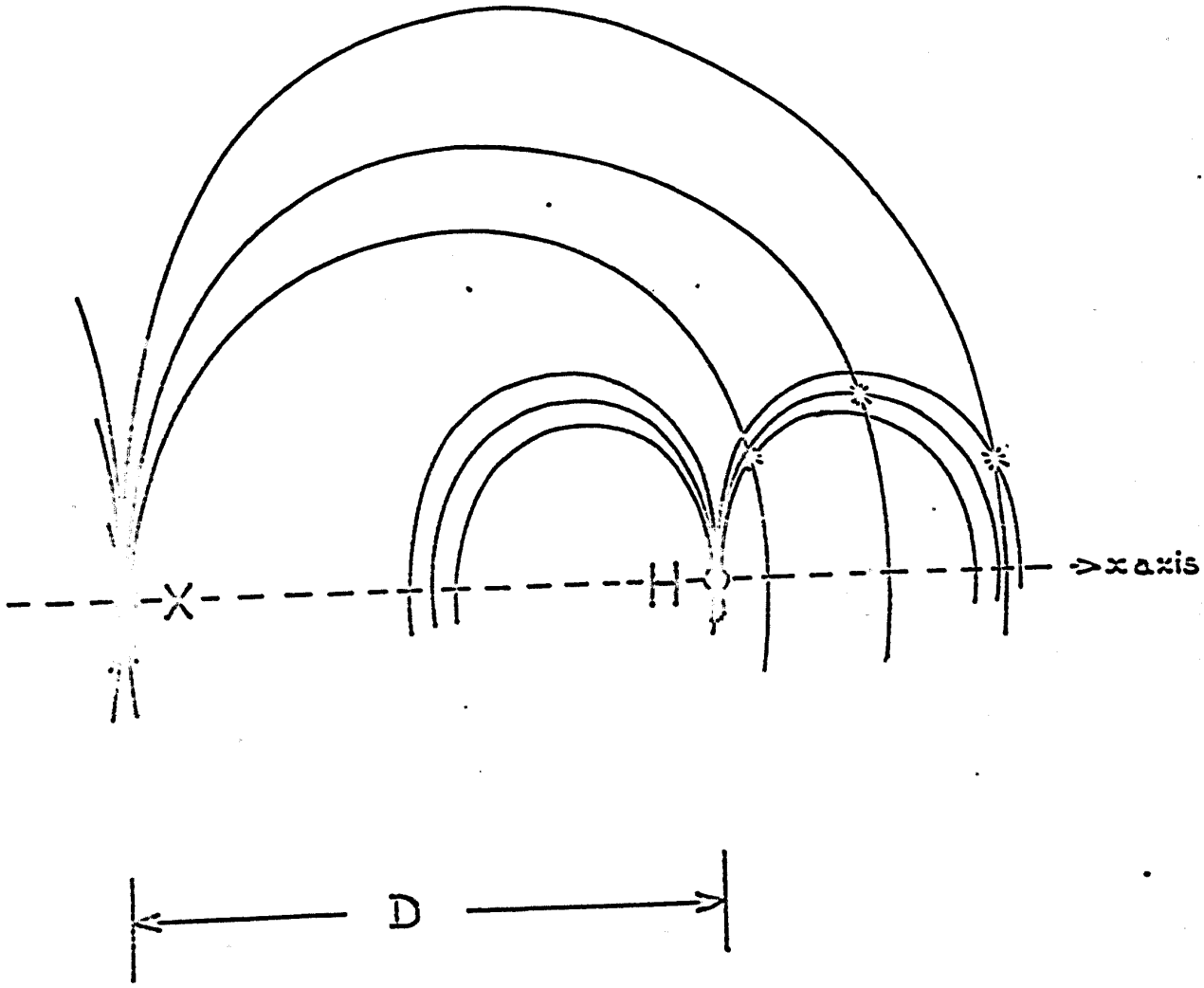


FIGURE 20. Formation of the antibinding region behind the proton in HX by the overlap of lines of constant force.

I. CALCULATION OF THE BINDING AND ANTIBINDING REGIONS.[1]

The boundary which separates the binding and antibinding regions in a diatomic molecule is such that a negative charge situated on it exerts equal force components along the bond axis on both nuclei. The equation

$$\frac{Z_\alpha \cos\theta_\alpha}{R_\alpha^2} = F_\alpha \qquad \text{(i)}$$

defines a curve along which the force components on a point charge assumes the constant value F_α, and the boundary between the binding and antibinding regions is thus given by

$$\frac{Z_\alpha \cos\theta_\alpha}{R_\alpha^2} = \frac{Z_\beta \cos\theta_\beta}{R_\beta^2} = F. \qquad \text{(ii)}$$

Figure 20 shows sections of the families of force lines on the nuclei of a hydride molecule for three values of F, with $Z_\alpha/Z_\beta = 8$. In the region between the nuclei the force components are always towards each other, leading to a binding effect (as previously pointed out by Berlin (15)). Behind the proton there is a small region, on the boundary of which corresponding curves of the two families intersect. Three points on this boundary are shown. A negative charge placed in this antibinding

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1. This approach to the interpretation and calculation of the boundary curves was the idea of Mr. P. Sefton, whom I wish to thank.

region causes the nuclei to draw apart. There is also an antibinding region behind the X nucleus, on the boundary of which F takes relatively small values. This region is large compared with that behind the proton (for this value of Z_α/Z_β), and a considerable part of its boundary is almost perpendicular to the X-H bond. Figure 19 shows such a boundary for hydrogen fluoride.

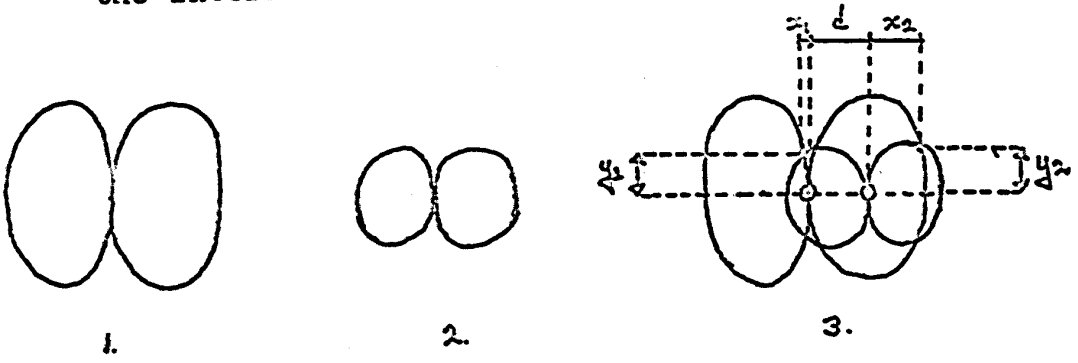
The equation of the boundary for a diatomic molecule is given in a standard Cartesian form in (97). It is very difficult to calculate the boundary using this representation. However, the parametric form (ii) leads to an extremely simple graphical procedure for determining the boundary which requires only a minimum amount of calculation. This procedure may be described briefly as follows:

(a) Plot the curve

$$\left.\begin{array}{ll} & R = \pm\sqrt{\cos\theta} \\ \text{.....} & R = \pm\sqrt{(Z_\alpha/Z_\beta)\cos\theta} \end{array}\right\} \text{for} -\frac{\pi}{2} \leq \theta \leq \frac{\pi}{2}$$

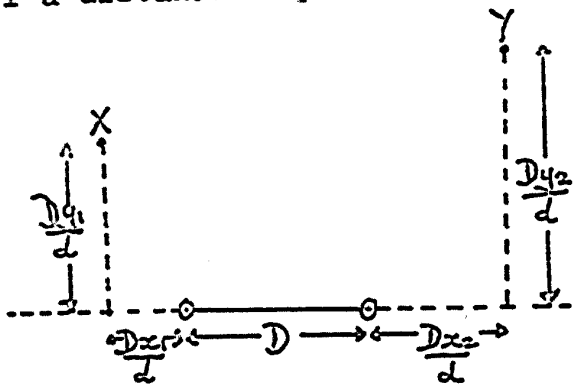
on polar paper. Trace these onto separate sheets of squared paper (curves 1 and 2).

(b) Overlay curve 1 on curve 2 with the x axes coincident and the origins a distance d apart (curve 3). Read the distances d, x_1, x_2, y_1 and y_2. Calculate $D(x_1/d)$, $D(x_2/d)$, $D(y_1/d)$ and $D(y_2/d)$, where D is the internuclear distance.



1. 2. 3.

(c) Plot the points X, Y as shown in 4, with the two nuclei a distance D apart.



Repeat from step (b) with differing values of d. The sets of X and Y points thus generated trace out the two required boundaries.

II. CALCULATION OF THE FORCES.

All of the force integrals are of the form $\int \mathcal{D}_{ax} \phi_i \phi_j \, d\tau$ where $\mathcal{D}_{ax}$ is the x component of the electric field due to nucleus a and is given by $\cos\theta_a / r_a^2$ in atomic units. ϕ_i and ϕ_j are atomic orbitals situated on one or both nuclei. The three types of force integrals needed to describe the force on nucleus a are designated as follows:

(a) When both orbitals are located on nucleus a, the integrals are designated $A(\phi_i, \phi_j)$, since they describe atomic forces.

(b) When both orbitals are situated on nucleus β, the integrals are termed $P(\phi_i, \phi_j)$, since they are of the penetration type.

(c) When one orbital is on nucleus a and the second on nucleus β, overlap type integrals appear, $0(\phi_i, \phi_j)$. The first orbital in the bracket ϕ_i, always refers to the atomic orbital on nucleus a.

HYDROGEN FLUORIDE

(a) With inner shell polarization.

Force on the fluorine nucleus (omitting a factor of nine, the nuclear charge of fluorine).

$$F(\psi_0^2) = 4\,[c_1 c_3\, A(1s,p) + c_2 c_3\, A(s,p)]$$

$$F(\psi_1^2) = -4 \cos\varepsilon_1 \sin\varepsilon_1\, A(s,p)$$

$$F(\psi_b^2) = 4\lambda^2 \cos\varepsilon_b \sin\varepsilon_b N_q(A[s;p] - q\, A[1s,p])$$

$$+ 4\lambda\mu[\cos\varepsilon_b N_q(O[s;h] - q\, O[1s,h])$$

$$+ \sin\varepsilon_b(O[p,h] - S_1 A[1s,p])]$$

$$+ 2\mu^2[P[h,h] - 2 S_1 O[1s,h]]$$

Force on the hydrogen nucleus.

$$F(\psi_o^2) = 2[c_1^2 P[1s,1s] + c_2^2 P[s;s'] + c_3^2 P[p,p]$$

$$+ 2c_1 c_2 P[1s,s'] + 2 c_1 c_3 P[1s,p] + 2 c_2 c_3 P[s;p]]$$

$$F(\psi_1^2) = 2\cos^2\varepsilon_1 P[s,s] + 2\sin^2\varepsilon_1 P[p,p]$$

$$- 4\cos\varepsilon_1 \sin\varepsilon_1 P[s,p]$$

$$F(\psi_b^2) = 2\lambda^2[\cos^2\varepsilon_b N_q^2(P[s;s'] + q^2 P[1s,1s] - 2q P[1s,s'])$$

$$+ \sin^2\varepsilon_b P[p,p] + 2\cos\varepsilon_b \sin\varepsilon_b N_q(P[s,p] - q P[1s,p])]$$

$$+ 4\lambda\mu[\cos\varepsilon_b N_q (O[h,s'] - q\, O[h,1s] - S_1 P[1s,s']$$

$$+ S_{1q} P[1s,1s]) + \sin\varepsilon_b(O[h,p] - S_1 P[1s,p])]$$

$$+ 2\mu^2[S_1^2 P[1s,1s] - 2 S_1 O[h,1s]]$$

$$2F(\psi_\pi^2) = 4 P(p_\pi, p_\pi)$$

(b) With valence shell polarization.

When $3d_\pi$ is included, the only force altered is that due to the π orbitals. If

$$\psi_\pi = N(p_\pi + c_5 d_\pi)$$

$$2F_F(\psi_\pi^2) = 4N^2 c_5 A(p_\pi, d_\pi)$$

$$2F_H(\psi_\pi^2) = 2N^2[P(p_\pi, p_\pi) + c_5^2 P(d_\pi, d_\pi) + 2c_5 P(p_\pi, d_\pi)]$$

When $3d_\sigma$ is included, the bond orbital force is altered. If the coefficient of $3d_\sigma$ in ψ_b is c_4,

$$F_F(\psi_b^2) = 4\lambda\sin\varepsilon_b [\lambda\cos\varepsilon_b A(s,p) + c_4 A(p,d)]$$
$$+ 4\mu[\lambda\cos\varepsilon_b O(s,h) + \lambda\sin\varepsilon_b(O(p,h) - S_1 A(p,1s)$$
$$+ c_4 O(d,h))] + 2\mu^2 [P(h,h) - 2S_1 O(1s,h)]$$

$$F_H(\psi_b)^2 = 2\lambda^2 [\cos^2\varepsilon_b P(s,s) + \sin^2\varepsilon_b P(p,p)$$
$$+ 2\cos\varepsilon_b\sin\varepsilon_b P(s,p)] + 4\lambda\mu[\cos\varepsilon_b(O(h,s) - S_1 P(1s,s)$$
$$+ \sin\varepsilon_b(O(h,p) - S_1 P(1s,p))]$$
$$+ 2\mu^2 [S_1^2 P(1s,1s) - 2S_1 O(h,1s)]$$
$$+ 2c_4^2 P(d,d) + 4c_4\mu O(h,d)$$

WATER.

All the forces calculated for hydrogen refer to the hydrogen atom labelled $H_{(1)}$. The component of the electric field, $\mathcal{D}_{\perp H}$ which appears in the integrals for the perpendicular forces on hydrogen is in the direction indicated for $F_{\perp}$ in Figure 12, except for the integrals $P[h'_2,h'_2]$ and $O[h'_1,h'_2]$. In these two latter integrals the field component was taken along the line joining the two hydrogens and the proper component of the resulting force ($\cos[\varepsilon/2]$) was then taken along the direction of $F_{\perp}$. These two integrals are primed for this reason. The three-centre integrals are the required components in the direction of the calculated forces. Their evaluation is discussed later in the Appendix.

$$
\begin{aligned}
F_{\perp}(\nu_{b1}^2) = {} & 2\lambda^2[2\cos\varepsilon_b \sin\varepsilon_b \sin\omega\, P[s,p_y] \\
& + 2\sin^2\varepsilon_b \cos\omega \sin\omega\, P[p_x,p_y]] + 2\mu^2[\delta^2 P'[h_2,h_2] \\
& - 2\delta O'[h_1,h_2]] + 4\lambda\mu[\sin\varepsilon_b \sin\omega\, O[h_1,p_y] \\
& - \delta(\cos\varepsilon_b\, P[s,h_2] + \sin\varepsilon_b \cos\omega\, P[p_x,h_2] \\
& + \sin\omega \sin\varepsilon_b\, P[p_y,h_2])]
\end{aligned}
$$

$$F_{\perp}(v_{b2}^2) = 4\lambda^2[\cos\varepsilon_b \sin\varepsilon_b \sin t\, P[s,p_y]$$
$$+ \sin^2\varepsilon_b \cos t \sin t\, P[p_x,p_y]] + 2\mu^2[P'[h_2,h_2]$$
$$- 2\delta O_H'[h_1,h_2]] + 4\lambda\mu[\cos\varepsilon_b P_H[s,h_2]$$
$$+ \sin\varepsilon_b (\cos t\, P_H[p_x,h_2] + \sin t\, P_H[p_y,h_2]$$
$$- \delta \sin t\, O_H[h_1,p_y])]$$

$$F_{\perp}(v_1^2) = 4[\sin^2\varepsilon_1 \sin[\varepsilon/2] \cos[\varepsilon/2] P[p_x,p_y]$$
$$- \sin\varepsilon_1 \cos\varepsilon_1 \sin[\varepsilon/2] P[s,p_y])]$$

The component of the electric field $\mathfrak{D}_{\parallel H}$ for the forces on hydrogen along the bond has the direction indicated by $F_{\parallel}$. This $\mathfrak{D}_{\parallel H}$ was employed in all the integrals but $P[h_2,h_2]$ and $O[h_1,h_2]$ which were calculated as in $F_{\perp}$ but multiplied by $\sin[\varepsilon/2]$ to obtain the proper component for $F_{\parallel}$.

$$F_{\parallel}(v_{b1}^2) = 2\lambda^2[\cos^2\varepsilon_b P[s,s] + \sin^2\varepsilon_b(\cos^2\omega P[p_x,p_x]$$
$$+ \sin^2\omega P[p_y,p_y]) + 2\cos\varepsilon_b \sin\varepsilon_b \cos\omega P[s,p_x]]$$
$$+ 2\mu^2[\delta^2 P[h_2,h_2] - 2\delta O[h_1,h_2]]$$
$$+ 4\lambda\mu[\cos\varepsilon_b O[h_1,s] + \sin\varepsilon_b \cos\omega O[h_1,p_x]$$
$$- \delta(\cos\varepsilon_b P[s,h_2] + \sin\varepsilon_b \cos\omega P[p_x,h_2]$$
$$+ \sin\varepsilon_b \sin\omega P[p_y,h_2])]$$

$$F_{\parallel}(\varphi_{b2}^2) = 2\lambda^2[\cos^2\varepsilon_b\, P[s,s] + \sin^2\varepsilon_b(\cos^2 t\, P[p_x,p_x] + \sin^2 t\, P[p_y,p_y]) + 2\cos\varepsilon_b \sin\varepsilon_b \cos t\, P[s,p_x]]$$
$$+ 2\mu^2[P[h_2',h_2] - 2\,\delta\, O[h_1'',h_2]]$$
$$+ 4\lambda\mu\,[\cos\varepsilon_b\, P[s,h_2] + \sin\varepsilon_b \cos t\, P[p_x,h_2] + \sin\varepsilon_b \sin t\, P[p_y,h_2] - \delta\cos\varepsilon_b\, O[h_1,s] - \delta\sin\varepsilon_b \cos t\, O[h_1,p_x]]$$

$$F_{\parallel}(\varphi_1^2) = 2[\cos^2\varepsilon_1\, P[s,s] + \sin^2\varepsilon_1(\cos^2[\varepsilon/2]\, P[p_x,p_x] + \sin^2[\varepsilon/2]\, P[p_y,p_y]) - 2\cos\varepsilon_1 \sin\varepsilon_1 \cos[\varepsilon/2]P[s,p_x]]$$

$$F_{\parallel}(\varphi_\pi^2) = 2P[p_z,p_z]$$

$$F_{\parallel}(\varphi_o^2) = 2\,P[1s,1s]$$

Forces on the oxygen nucleus.

It is most convenient in the calculation of the orbital contributions to F_0 to employ a number of different field components for $\mathfrak{D}_0$ in the calculation of the integrals. For those integrals which contain a 2p orbital $\mathfrak{D}_0$ was directed along the 2p orbital in question and the proper

component along F_0 then taken. For those involving the 1s and 2s orbitals $\mathfrak{D}_0$ was directed along the bond axis and the proper component again taken along F_0. As stated in the introduction a common factor of eight, the nuclear charge on oxygen, has been omitted from the expressions for F_0 and the nuclear repulsion. Thus $\mathfrak{D}_0$ is the electric field per unit charge in these formulae.

$$F_0(\psi_b^2) = 2\lambda^2[2\cos\varepsilon_b \sin\varepsilon_b \cos(\alpha/2) A(s,p_1)]$$
$$+ 2\mu^2 \cos(\varepsilon/2)[1 + \delta^2 - 2\delta S_1] P(h_i,h_i)$$
$$+ 4\lambda\mu[\cos(\varepsilon/2) \cos\varepsilon_b(1-\delta) O(s,h)$$
$$+ \sin\varepsilon_b (\cos(\varepsilon/2) O(p_x,h_1)(\cos\omega - \delta\cos t)$$
$$+ \sin(\varepsilon/2) O(p_y,h_1)(\sin\omega - \delta\sin t))]$$

$$F_0(\psi_1^2) = +4 \cos\varepsilon_1 \sin\varepsilon_1 A(s,p_{x'})$$

$$F_0(\psi_o^2) = -4N^2 c_3 A(1s,p_{x'})$$

where $p_{x'}$ is directed along the x' axis. The expression for $F_0(\psi_o{}^2)$ applies when ψ_o contains $p_{x'}$ character with coefficient c_3.

AMMONIA.

Forces on the hydrogen nuclei.

All the forces calculated for hydrogen refer to the atom labelled $H_{(1)}$. The component of the electric field $\mathfrak{D}_1$ which appears in the integrals for the perpendicular forces on hydrogen is in the direction indicated for F_1 in Figure 15, except for the integrals $P_H[h_2,h_2]$ and $O_H[h_1,h_2]$. In these two latter integrals the field component was taken along the line joining the two hydrogens and a component of the resulting force ($\sqrt{3}\cos\theta$) was then taken along the direction of F_1. These two integrals are primed for this reason. The $2p_x$, $2p_y$ and $2p_z$ atomic orbitals are designated x, y and z respectively.

$$F_1(\psi_{b1}^2) = 4\lambda^2[\cos\omega \sin\omega \sin^2\varepsilon_b P[x,z]$$

$$+ \sin\omega \cos\varepsilon_b \sin\varepsilon_b P[s,z]]$$

$$+ 2\mu^2[\delta^2(1+S_1) P'[h_1,h_2] - 2\delta O'[h_1,h_2]]$$

$$+ 4\lambda\mu[\sin\omega \sin\varepsilon_b O[h_1,z] - 2\delta\cos\varepsilon_b P[h_2,s]$$

$$- \sin\varepsilon_b(2\delta\cos\omega P[h_2,x] + 2\delta\sin\omega P[h_2,z])]$$

$$F_{\perp}(\varphi_{b2}^2) = F_{\perp}(\varphi_{b3}^2) = 4\lambda^2[\sin^2\varepsilon_b \mathcal{X} Z P(x,z)$$

$$+ \cos\varepsilon_b \sin\varepsilon_b Z P(s,z)]$$

$$+ 2\mu^2 [(1-2\delta S_1 + \delta^2) P'(h_2,h_2) - 2\delta(1-\delta) O'(h_1,h_2)]$$

$$+ 4\lambda\mu [\cos\varepsilon_b (1-\delta) P(h_2,s) + \sin\varepsilon_b \mathcal{X} (1-\delta) P(h_2,x)$$

$$+ \sin\varepsilon_b (Z(1-\delta) P(h_2,z) - \delta Z O(h_1,z))$$

$$+ \sin\varepsilon_b \mathcal{Y} (1+\delta) P(h_2,z)/(\sqrt{3}\cos\theta)]$$

$$F_{\perp}(\varphi_1^2) = 4[\sin^2\varepsilon_1 \cos\theta \sin\theta P(x,z) - \cos\varepsilon_1 \sin\varepsilon_1 \sin\theta P(s,z)]$$

$$\mathcal{Y} = (\sqrt{3}/2) \sin(\theta - \omega)$$

$$Z = \cos(\theta - \omega) \sin\theta + (1/2) \sin(\theta - \omega) \cos\theta$$

$$\mathcal{X} = \cos(\theta - \omega) \cos\theta - (1/2) \sin(\theta - \omega) \sin\theta$$

The component for the electric field $D_{\parallel}$ for the forces on hydrogen along the bond has the direction indicated by $F_{\parallel}$, except for the integrals $P(h_2,h_2)$ and $O(h_1,h_2)$ which were calculated as in $F_{\perp}$ but multiplied by $(\sqrt{3}/2) \sin\theta$ to obtain the proper component for $F_{\parallel}$.

$$F_{\parallel}(\vartheta_{b1}^2) = 2\lambda^2[\cos^2\varepsilon_b\, P(s,s) + \sin^2\varepsilon_b\,(\sin^2\omega\, P(z,z) + \cos^2\omega\, P(x,x)) + 2\cos\varepsilon_b \sin\varepsilon_b \cos\omega\, P(s,x)]$$
$$+ 4\lambda\mu\,[\cos\varepsilon_b\, O(h_1,s) + \sin\varepsilon_b \cos\omega\, O(h_1,x)$$
$$- 2\delta(\cos\varepsilon_b\, P(s,h_2) + \sin\varepsilon_b \cos\omega\, P(x,h_2)$$
$$+ \sin\varepsilon_b \sin\omega\, P(z,h_2))]$$
$$+ 4\mu^2\,[\delta^2(1+S_1)\,P'(h_2,h_2) - 2\,\delta\,O'(h_1,h_2)]$$

$$F_{\parallel}(\vartheta_{b2}^2) = F_{\parallel}(\vartheta_{b3}^2) = 2\lambda^2[\cos^2\varepsilon_b\, P(s,s)$$
$$+ \sin^2\varepsilon_b\,(\mathcal{X}^2\, P(x,x) + (\mathcal{Y}^2 + \mathcal{Z}^2)\, P(z,z))$$
$$+ 2\cos\varepsilon_b \sin\varepsilon_b\, \mathcal{X}\, P(s,x)]$$
$$+ 4\lambda\mu[(1-\delta)(\cos\varepsilon_b\, P(s,h_2) + \sin\varepsilon_b \mathcal{X}\, P(x,h_2)$$
$$+ \sin\varepsilon_b\, \mathcal{Z}\, P(z,h_2)) - \delta(\cos\varepsilon_b\, O(h_1,s)$$
$$+ \sin\varepsilon_b\, \mathcal{X}\, O(h_1,x)) + (1+\delta)\sin\varepsilon_b\, \mathcal{Y}\, P(z,h_2)/(\sqrt{3}\cos\theta)]$$
$$+ 2\mu^2\,[P'(h_2,h_2)(1+\delta^2 - 2\delta S_1)$$
$$- 2\,\delta\,O'(h_1,h_2)(1-\delta)]$$

$$F_{\parallel}(\varphi_1^2) = 2[\cos^2\varepsilon_1\, P[s,s] + \sin^2\varepsilon_1(\sin^2\theta\, P[z,z] + \cos^2\theta\, P[x,x]) - 2\cos\varepsilon_1 \sin\varepsilon_1 \cos\theta\, P[s,x]]$$

$$F_{\parallel}(\varphi_o^2) = 2\, P[1s,1s]$$

Force on the nitrogen nucleus.

The field component for the atomic force integrals is directed along the $\mathcal{Z}$ axis and in the remaining integrals is directed along F_N.

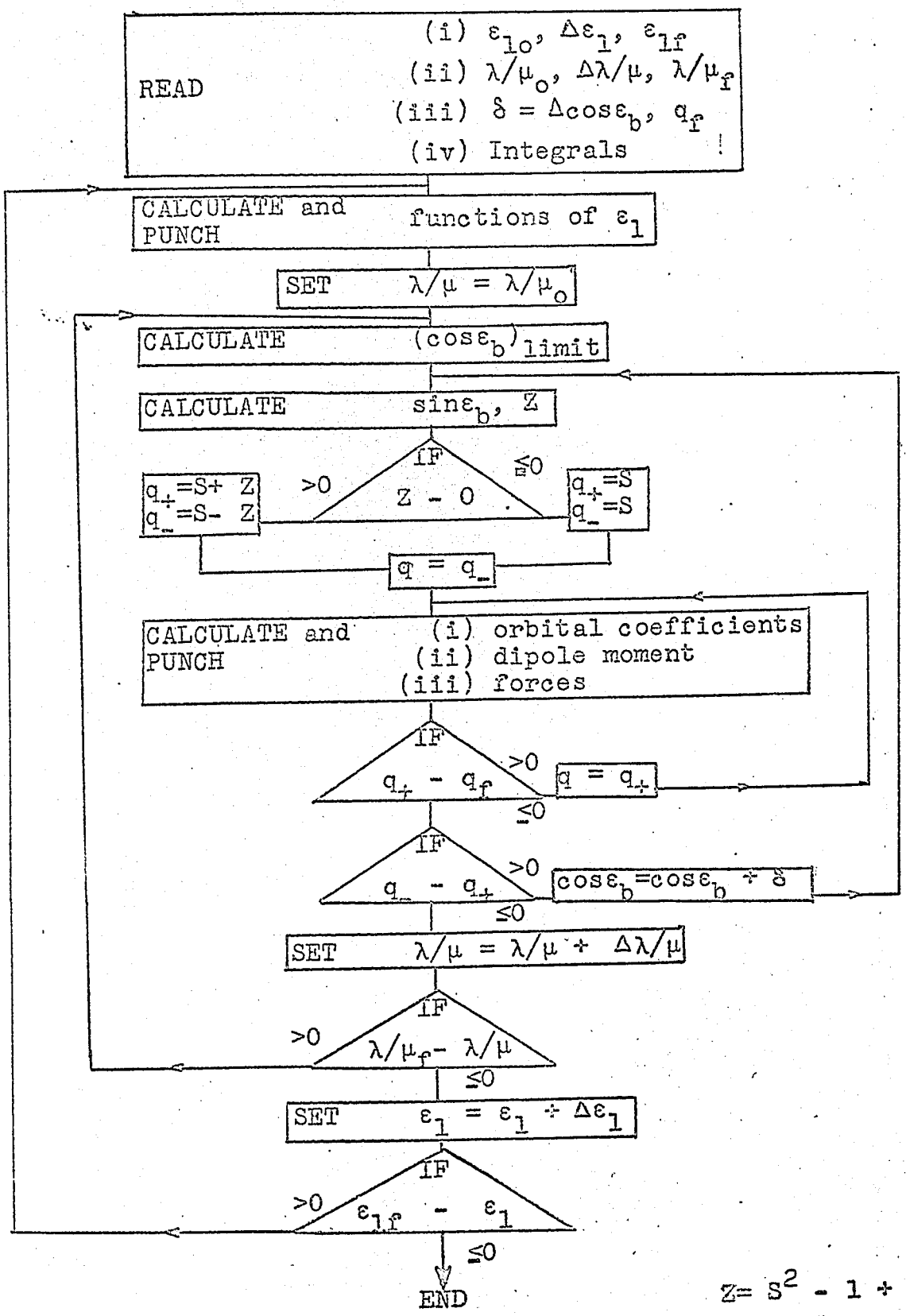
$$F_N(\varphi_{bi}^2) = 4\lambda^2 \cos\varepsilon_b \sin\varepsilon_b \cos[\theta-\omega]\, A[\mathcal{Z},s] + 4\lambda\mu\,[\cos\varepsilon_b \cos\theta\,[1-2\delta]\, O[h_1,s] + \sin\varepsilon_b \cos\theta\,(\cos\omega - 2\delta\mathcal{X})\, O[h_1,x] + \sin\varepsilon_b \sin\theta\,(\sin\omega - 2\delta\mathcal{Z})\, O[h_1,z] + 2\mu^2\,[\cos\theta(1 + 2\delta^2 + 2\delta S_1\,[\delta-2])\, P[h_i,h_i]]$$

$$F_N(\varphi_1^2) = -4\cos\varepsilon_1 \sin\varepsilon_1\, A[\mathcal{Z},s]$$

$$F_N(\varphi_o^2) = +4\, c_3\, A[\mathcal{Z},1s]$$

PROGRAM 1.

Forces in hydrogen fluoride including inner shell polarization.



$$Z = S^2 - 1 + 1/N_q^2$$

DATA AND RESULTS FOR HYDROGEN FLUORIDE WITH INNER SHELL POLARIZATION.

$$\psi_o = c_1\ 1s + c_2\ s' + c_3\ p$$

$$\psi_b = b_1\ 1s + b_2\ s' + b_3\ p + \mu h$$

$$\psi_1 = d_1\ 1s + d_2\ s' + d_3\ p$$

DATA

(1)	ε_1(radians)	$\Delta\varepsilon_1$	ε_{1f}(radians)
(2)	q_f	$\Delta\cos\varepsilon_b$	
(3)	λ/μ_o	$\Delta\lambda/\mu$	λ/μ_f

INTEGRALS

(4)	S(h,1s)	S(h,s')	S(h,s)	S(h,p)	S(1s,s')		- Overlaps
(5)	A(1s,p)	A(s',p)	O(1s,h)	O(2p,h)	O(s',h)	P(h,h)	- F_F
(6)	1s|Z|p	s'|Z|p	1s|Z|h	2p|Z|h	s'|Z|h	R	- Dipole
(7)	P(1s,1s)	P(s',s')	P(p,p)	$P(p_\pi, p_\pi)$	P(p,s')		- F_H
(8)	P(p,1s)	P(s',1s)	O(h,1s)	O(h,p)	O(h,s')		

RESULTS

(1)	ε_1	$\cos\varepsilon_1$	$\sin\varepsilon_1$	d_1	d_2	d_3	
(2)	$\cos\varepsilon_b$	$\sin\varepsilon_b$	c_1	N_q	q	c_3/c_1	c_2/c_1
(3)	c_1	c_2	c_3	b_1	b_2	b_3	
(4)	λ/μ	λ	μ	$D(\psi_o^2)$	$D(\psi_1^2)$	$D(\psi_b^2)$	D
(5)	Force on F: $F(\psi_o^2)$	$F(\psi_1^2)$	$F(\psi_b^2)$	[$F(\psi_{bH}^2)$	$F(\psi_{bF}^2)$	$F(\psi_{bo}^2)$]	$F_F(e)$
(6)	Force on H: $F(\psi_o^2)$	$F(\psi_1^2)$	$F(\psi_b^2)$	[$F(\psi_{bF_1}^2)$	$F(\psi_{bF_2}^2)$	$F(\psi_{bo}^2)$]	$F_H(e)$

(1) -10471976 50 -10000000 40 -10471976 50

(2) 29000000 49 -78150000 48

(3) 16845000 51 10000000 48 16845000 51

(1) 48704700 49 43880500 50 43956800 50 33468700 50 23322147 50

(2) 92557070 51 39392110 51 27544000 50 11783310 51 48770100 50 83330800 50

(3) 50954800 49 55189200 50 33299000 48 47285400 50 30715700 50 17330000 51

(4) 10000000 51 93997900 50 12698560 51 76768300 50 54178400 50

(5) 58803400 49 23320900 50 54979300 49 73485500 50 59306500 50

(1) -60000000 51 99452186 50 -10452846 50 -23852140 50 10227249 51 10452846 50

(2) -38690561 50 92211935 50 99930428 50 10066818 51 30338600 49 69611066 49 -75239002 48

(3) 99930428 50 -75186657 48 69562636 49 -13865825 49 -31588363 50 74785432 50

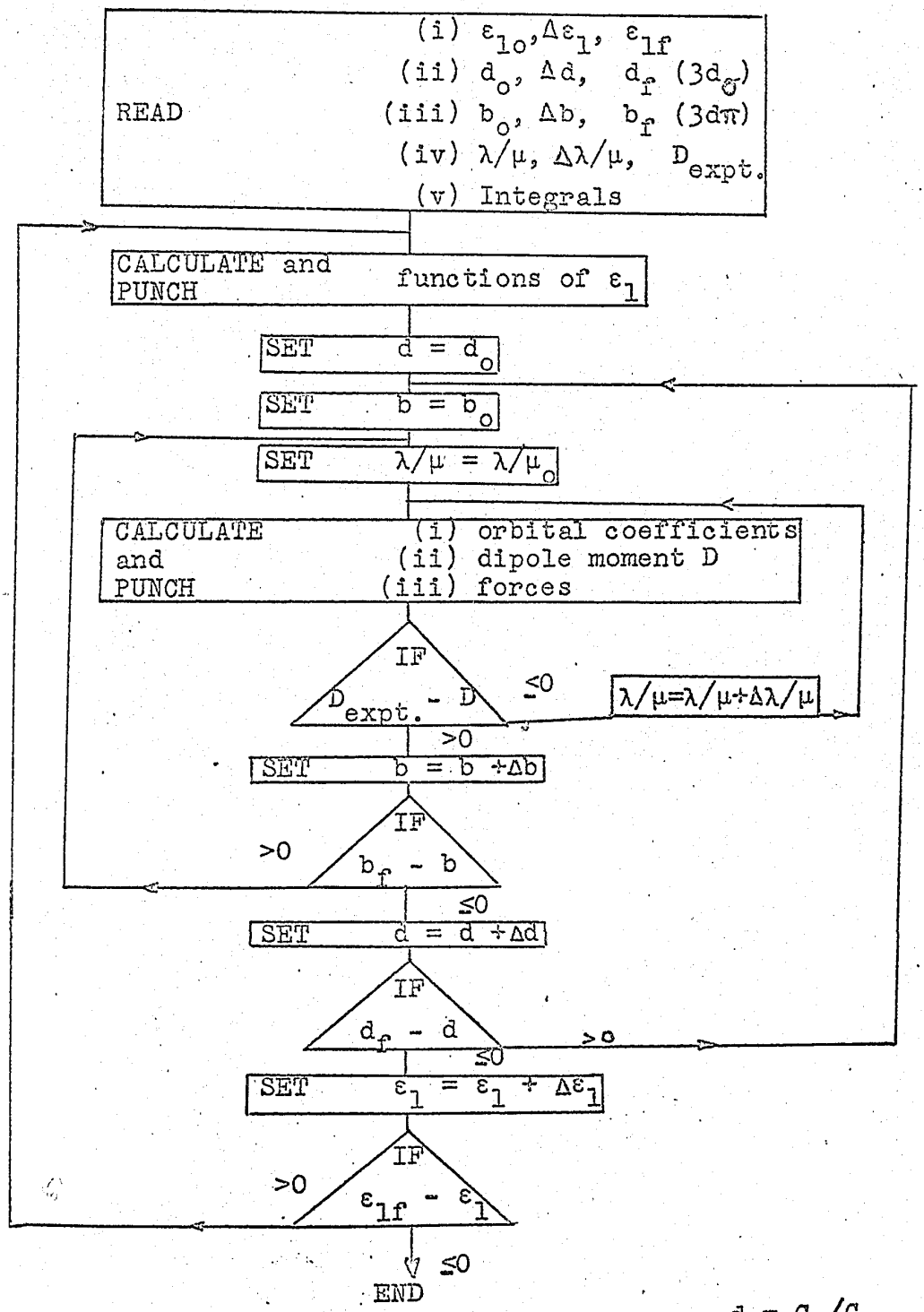
(4) 16845000 51 81101684 50 48145850 50 13013738 49 23091586 50 77388870 50 71518170 50

(5) 23088354 52 68526371 51 -20941773 52 34769286 51 -36956066 52 12537364 52 89992180 51

(6) 20178224 51 51768922 51 17942074 51 -51030652 50 16083969 51 69611704 50 89889220 51

PROGRAM 2.

Forces in hydrogen fluoride including $3d_\sigma$ and $3d_\pi$ polarization.



$d = c_4/c_1$

$b = c_5/c_1$

DATA AND RESULTS FOR HYDROGEN FLUORIDE WITH 3d POLARIZATION.

DATA

(1)	ε_1 (radians)	$\Delta\varepsilon_1$	ε_{1f}	} Not shown			
(2)	d	Δd	d_f ($3d_\sigma$)				
(3)	b	Δb	b_f ($3d_\pi$)				
(4)	λ/μ	$\Delta\lambda/\mu$	λ/μ_f				
(5)	S(1s,h)	S(s',h)	S(s,h)	S(p,h)	S(1s,s')	S(1s,d)	- Overlaps
(6)	A(1s,p)	A(s',p)	O(1s,h)	O(p,h)	O(s',h)	$P(h_2,h_2)$	- F_F
(7)	1s|Z|p	1s|Z|s'	1s|Z|h	p|Z|h	s'|Z|h	R	- Dipole
(8)	P(1s,1s)	P(s',s')	P(p,p)	$P(p_\pi,p_\pi)$	P(p,s')		} - F_H
(9)	P(p,1s)	P(s',1s)	O(h,1s)	O(h,p)	O(h,s')		
(10)	A(d,p)	P(d,d)	P(d,s')	P(d,1s)	P(d,p)	O(d,h) O(h,d)	} - $3d_\sigma$ and
(11)	A(d_π, p_π)	$P(d_\pi, d_\pi)$	$P(d_\pi,p_\pi)$	d|Z|p	d|Z|h	d_π|Z|p_π -	} $3d_\pi$

RESULTS

(1)	ε_1	$\cos\varepsilon_1$	$\sin\varepsilon_1$	d_1	d_2	d_3	N_o
(2)	$\cos\varepsilon_b$	$\sin\varepsilon_b$	b_1	b_2	b_3	d	b
(3)	λ/μ	λ	μ	$D(\varphi_\pi)$	$D(\varphi_1)$	$D(\varphi_b)$	D
(4)	Force on F: $F(\varphi_\pi)$	$F(\varphi_1)$	$F(\varphi_b)$	[$F(\varphi_{bH})$	$F(\varphi_{bF})$	$F(\varphi_{bo})$]	$F_F(e)$
(5)	Force on H: $F(\varphi_\pi)$	$F(\varphi_1)$	$F(\varphi_b)$	[$F(\varphi_{bF_1})$	$F(\varphi_{bF_2})$	$F(\varphi_{bo})$]	$F_H(e)$

[illegible] π [illegible]

DATA

(3)	10000000 49	10000000 48	10000000 49
(4)	16600000 51	10000000 48	16600000 51

[illegible] (in units of $1/10^8$)

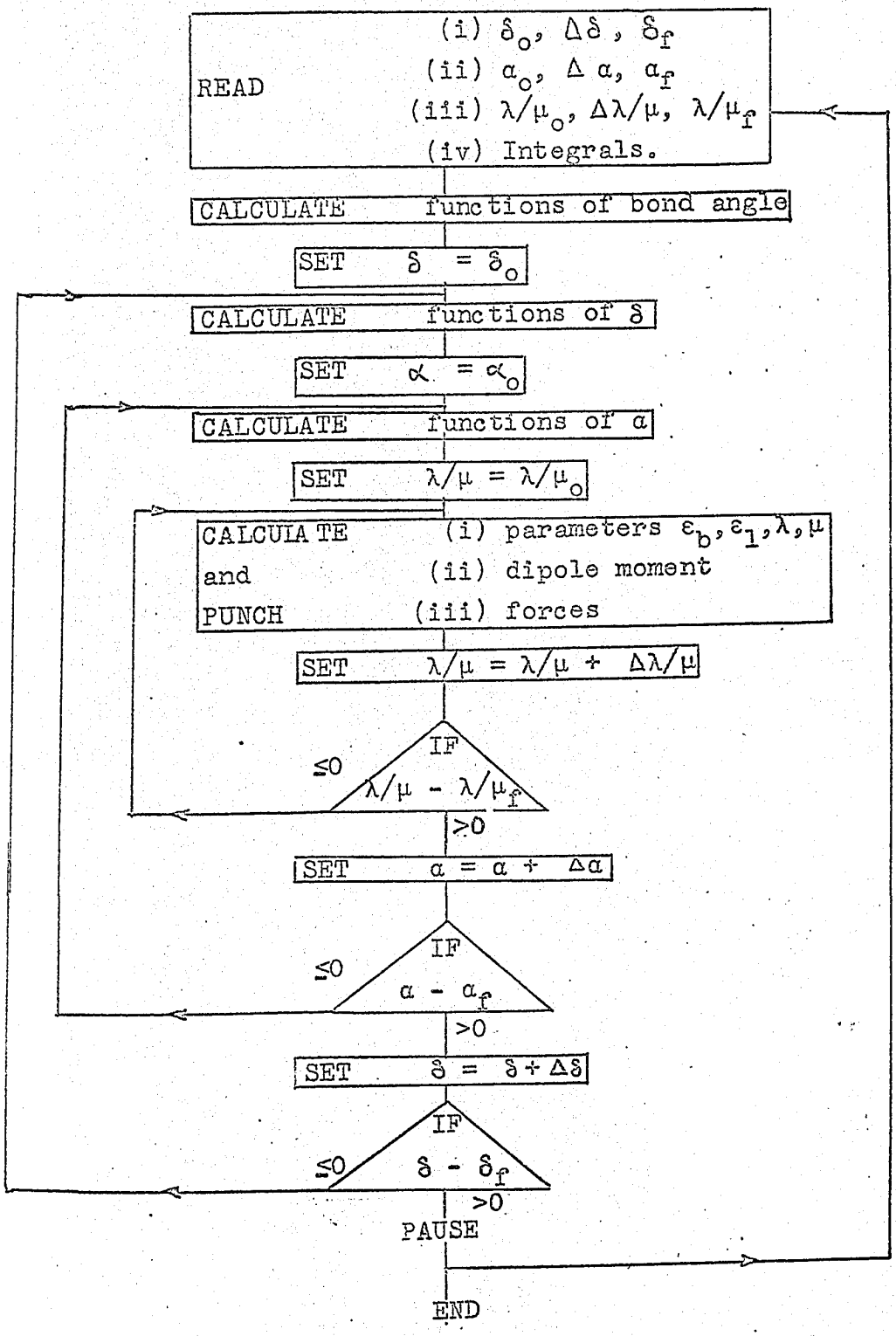
(5)	48704700 49	43880500 50	43956800 50	33468700 50	23322147 50	30878300 50	
(6)	92557070 51	39392110 51	27544000 50	11783310 51	48770100 50	83330800 50	
(7)	50954800 49	55189200 50	33299000 48	47285400 50	30715700 50	17330000 51	
(8)	10000000 51	93997900 50	12698560 51	76768300 50	54178400 50		
(9)	58803400 49	23320900 50	54979300 49	73485500 50	59306500 50		
(10)	18818100 51	12357930 51	36562300 50	82476400 48	68481900 50	77212600 50	66268100 50
(11)	15773570 51	64706700 50	25403200 50	52883900 50	60764600 50	45798800 50	

RESULT

(2)		10000000 51		-23983526 50	10283584 51		10283584 51
(3)	-26480000 50	96430338 50	26922946 49	-21456705 50	75982616 50		10000000 49
(4)	16600000 51	78795343 50	47467074 50	36635376 49		98240190 50	71396270 50
(5)	11355834 51		71383390 50	33795819 51	-16303760 52	13638012 52	18494173 51
(6)	30910043 51	18730656 51	20217259 51	-35389319 50	15542678 51	82135132 50	89857958 51

PROGRAMS 3 AND 4.

Flow chart for the forces in water and in ammonia.



DATA AND RESULTS FOR WATER.

DATA

(1)	$\mathcal{S}_o$	$\Delta\mathcal{S}$	$\mathcal{S}_f$	ε(radians)
(2)	α_o(radians)	$\Delta\alpha$	α_f	
(3)	λ/μ_o	$\Delta\lambda/\mu$	λ/μ_f	

INTEGRALS

(4)	$P(s,y)$	$P(x,y)$	$P'(h_2h_2)$	$0(h_1,y)$	$0'(h_1,h_2)$		$-F_\perp$
(5)	$S(h_1,h_2)$	$S(s,h_i)$	$S(x,h_i)$	$P(h_2,y)$	$P(h_2,s)$	$P(h_2,x)$	$-F_\perp$
(6)	$P(s,s)$	$P(s,x)$	$P'(h_2,h_2)$	$P(x,x)$	$P(y,y)$	$0'(h_1,h_2)$	$-F_\parallel$
(7)	$0(h,s)$	$0(h_1,x)$	$P(h_2,y)$	$P(h_2,s)$	$P(h_2,x)$		$-F_\parallel$
(8)	$s\|X'\|X'$	$s\|X'\|h_1$	$y\|X'\|h_1$	$x\|X'\|h_1$			$-D$
(9)	$A(s,x')$	$0(s,h)$	$0(y,h_1)$	$0(x,h_1)$	$P(h_1,h_1)$		$-F_0$

RESULTS

(1)	$\mathcal{S}$	α	ω	θ	λ/μ	λ	μ
(2)	ε_b	ε_ℓ	$F_1(\psi_\ell^2)$	$F_1(\psi_{b1}^2)$	$F_1(\psi_{b2}^2)$	$\Sigma F_\perp$ (1 electron)	F_e-F_n
(3)	$\cos\omega$	$\sin\omega$	$F_\parallel(\psi_\ell)$	$F_\parallel(\psi_{b1}^2)$	$F_\parallel(\psi_{b2}^2)$	$\Sigma F_\parallel$ (1 electron)	F_e-F_n
(4)	$\cos\varepsilon_b$	$\sin\varepsilon_b$	D_ℓ	D_{bA}	D_{bB}	D	
(5)	$\cos\varepsilon_\ell$	$\sin\varepsilon_\ell$	$F_0(\psi_\ell)$	$F_0(\psi_{bA}^2)$	$F_0(\psi_{bB}^2)$	ΣF_0 (1 electron)	F_e-F_n

(6) Data for checking program.

8

(1)	50000000 50	10000000 48	50000000 50	18229964 51			
(2)	10297443 51	10000000 48	10297443 51				
(3)	15140000 51	10000000 48	15140000 51				
R1 (4)	10079000 50	68318700 49	73365100 49	10955300 50	32795700 49		
(5)	21821000 50	45744900 50	39447500 50	49962000 49	30064000 49	12473000 49	
R2 (6)	27194300 50	16643300 50	94667600 49	38056400 50	22778200 50	42318300 49	
(7)	18408700 50	23424400 50	55147000 49	85669000 49	25084000 49		
D (8)	63950000 50	36935100 50	27293500 50	60185500 50			
D (9)	48773600 50	13403900 50	14100700 50	33649700 50	26110300 50		

(1)	50000000 50	59000002 52	22724999 52	15050000 53	15140000 51	73652142 50	48647386 50
(8)	98549198 52	14707782 50	-40856968 47	36873030 49	-12901190 48	35174341 49	-44709060 48
(3)	92236963 50	38630851 50	27141969 50	28646081 50	16430443 50	72218493 50	-28060100 49
(4)	-14865876 50	98888856 50	65663374 48	35508787 50	-18570756 51	72205420 50	28511080 50
(5)	99999673 50	25669894 48	-25040181 48	-13540980 50	30065974 50	16274592 50	-48466430 49
(6)	30805462 49	51236997 49	44440475 49	58183044 49	21220602 09	21020622 59	21225602 59

DATA AND RESULTS FOR AMMONIA

DATA

(1)	δ_o	$\Delta\delta$	δ_f	ε(radians)
(2)	α_o(radians)	$\Delta\alpha$	α_f	
(3)	λ/μ_o	$\Delta\lambda/\mu$	λ/μ_f	

INTEGRALS

$F_\perp$	(4)	$P(s,z)$	$P(x,z)$	$P'(h_2,h_2)$	$O(h_1,z)$	$\Theta'(h_1,h_2)$		
	(5)	$S(h_1,h_2)$	$S(s,h)$	$S(x,h_1)$	$P(z,h_2)$	$P(s,h_2)$	$P(x,h_2)$	$\left(\frac{P(z,h_2)}{\cos\theta}\right)$
$F_\parallel$	(6)	$P(s,s)$	$P(x,s)$	$P'(h_1,h_2)$	$P(x,x)$	$P(z,z)$	$O'(h_1,h_2)$	
	(7)	$O(h_1,s)$	$O(h_1,x)$	$P(z,h_2)$	$P(s,h_2)$	$P(x,h_2)$		
D	(8)	$s\|Z\|p$	$s\|Z\|h_i$	$z\|Z\|h_1$	$x\|Z\|h_1$			
F_N	(9)	$A(s,\mathbb{Z})$	$O(s,h_i)$	$O(z,h_1)$	$O(x,h_1)$	$P(h_i,h_i)$		

RESULTS

(1)	δ	α	ω	θ	λ/μ	λ	μ
(2)	ε_b	ε_1	$F_\perp(\psi_\ell^2)$	$F_\perp(\psi_{b1}^2)$	$2F_\perp(\psi_{b2}^2)$	$\Sigma F_\perp$(1 electron)	F_e-F_n
(3)	$\cos\omega$	$\sin\omega$	$F_\parallel(\psi_\ell^2)$	$F_\parallel(\psi_{b1}^2)$	$2F_\parallel(\psi_{b2}^2)$	$\Sigma F_\parallel$(1 electron)	F_e-F_n
(4)	$\cos\varepsilon_b$	$\sin\varepsilon_b$	D_ℓ	D_{bA}	D_{bB}	D	
(5)	$\cos\varepsilon_1$	$\sin\varepsilon_1$	$F_N(\psi_\ell^2)$	$F_N(\psi_{bA}^2)$	$F_N(\psi_{bB}^2)$	ΣF_N(1 electron)	F_e-F_n
(6)	[Data to check program]					$\mathcal{X}$	$\mathcal{Z}$

(1)	28000000 50	10000000 48	28000000 50	18727383 51			
(2)	11772246 51	10000000 48	11772246 51				
(3)	13740000 51	10000000 48	13740000 51				
(4)	96582000 49	69135000 49	66613200 49	11093800 50	27981300 49		
(5)	19438700 50	48682800 50	44431600 50	13408000 49	15228000 49	55076000 48	36480000 49
(6)	23567500 50	14492300 50	84278200 49	32889400 50	19214100 50	35401800 49	
(7)	16238100 50	20848100 50	27527000 49	75355000 49	16795000 49		
(8)	74595200 50	45981000 50	32590200 50	73693000 50			
(9)	36743400 50	10385900 50	11951200 50	28723900 50	23918200 50		
(1)	28000000 50	67450001 52	28562433 52	14012624 53	13740000 51	70135579 50	51044817 50
(2)	98804841 52	19993147 50	-62615140 47	52572513 49	-18288074 49	33658288 49	-28819300 47
(3)	87829666 50	47811608 50	23530294 50	22586168 50	29183502 50	75299964 50	-42840700 49
(4)	-15306939 50	98821542 50	10411800 49	51116837 50	-20486519 51	57340270 50	19105490 49
(5)	99999387 50	34894553 48	-25642733 48	-12589325 50	26287546 50	13441794 50	-34995250 49
(6)	11247887 49	11060949 49	27912093 49	22620818 49	30729981 49	-16043940 49	83155723 50

(10) Hartree's parameters. $\zeta_{1s} = 1.03$; ζ_{2s} by Slater's rule = 1.016 a.u.

Σ_1 (4)	95183000 49	67756000 49	64858000 49	10451000 50	35130000 49			
Σ_1 (5)	33359000 50	54192000 50	40405000 50	15216000 49	15112000 49	70129000 48	40560000 49	
Σ_{11} (6)	23388000 50	14372000 50	80130000 49	32617000 50	19073000 50	43401000 49		
Σ_{11} (7)	15253000 50	17840000 50	25194000 49	86710000 49	27491000 49			
D (8)	74595000 50	44084000 50	41464000 50	74489000 50				
P_{11} (9)	36743000 50	10725000 50	11948000 50	28724000 50	20055000 50			

(11) $\theta = 111.9°$, electrostatic orbital exponents. $\zeta_{1s} = 1.03$; $\zeta_{2s} = 1.005$ a.u.

Σ_1 (4)	96562000 49	69135000 49	41818600 49	11093800 50	16543800 49			
Σ_1 (5)	17485800 50	48682800 50	44431600 50	65782000 48	98483000 48	36824000 48	26382000 49	
Σ_{11} (6)	23567500 50	14492300 50	81207400 49	32889400 50	19214100 50	32126200 49		
Σ_{11} (7)	16238100 50	20848100 50	18906000 49	72524000 49	92877000 48			
D (8)	74595200 50	45981000 50	32590200 50	73693000 50				
P_{11} (9)	36743400 50	10385900 50	11951200 50	28723900 50	23918200 50			

(i) Lehr. Hilton and Uhrig's parameters. $\theta = 120^{\circ}$. $\zeta_x = 1.0$ ζ_y by Lehr's rules.

P_1	(4)	10079000 50	68318700 49	48368200 49	10363000 50	25813400 49	
	(5)	32237800 50	50873800 50	34798700 50	45948000 49	21629000 49	73825000 48
P_0	(8)	63950400 50	33360000 50	35615000 50	59965000 50		
	(9)	48773500 50	12732100 50	12595400 50	35931900 50	21390600 50	

(ii) Lehr. Unsatisfactory parameters. $\theta = 109^{\circ}28'$. $\zeta_x = 1.00$. ζ by Lehr's rules.

P_1	(4)	10079000 50	68318700 49	65023800 49	10955300 50	27863100 49	
	(5)	20156900 50	45744900 50	39447500 50	46442000 49	27375000 49	94360000 48

(iii) Hilton-Uhrig. Parameters determined by empirical rule. $\zeta_{(b)} = 2.34$ $\zeta_{(1a)} = 0.70$ $\zeta_{(a)} = 2.66$ $\zeta_{(p)} = 2.66$

S	(4)	47641500 49	41858800 50	41979200 50	33821300 50	24638800 50	
P_1	(5)	91895000 51	40899680 51	28477700 50	11684710 51	48897100 50	84156700 50
D	(6)	50088900 49	54262200 50	33550000 48	47570000 50	28605000 50	18100000 51
P_{II}	(7)	10000000 51	95202000 50	12696730 51	79319400 50	54034800 50	
	(8)	57765700 49	24638700 50		70680800 50	58886000 50	

III. CALCULATION OF FORCE INTEGRALS.

(A).. Three-centre integrals.

A number of three-centre integrals occur in the force calculations. For the forces on h_i they are $P_H(2s,h_j)$, $P_H(2p_x,h_j)$ and $P_H(2p_y,h_j)$ for both the parallel and perpendicular cases. Bader (69) has published a method for evaluating these integrals. The method employs a series expansion centred on the central atom for $\mathfrak{D}_{\perp H}$ and $\mathfrak{D}_{\parallel H}$ in terms of Gegenbauer polynomials coupled with the method of Coulson and Barnett (68) for the expansion of the 1s orbital h_j on the same central atom. Since six such integrals had to be evaluated for a number of bond parameters a numerical method employing an IBM 650 computer was also developed[1] for their evaluation. The two methods gave good agreement. For example, $P_H(2p_y,h_j)$ for the perpendicular case when evaluated by the expansion method was found to be equal to 0.050331 a.u. and by the machine method to equal 0.049962 a.u.

There is one 3-centre integral involved in the calculation of F_X. It is $P_X(h_i,h_j)$, the force on the heavy nucleus due to the overlap charge density between

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1. Thanks are due to Miss O. Bosko for her assistance and analysis of this problem. The program she wrote for the $P_{H\parallel}$ integrals was subsequently modified for the $P_{H\perp}$ integrals and for the three centre integrals occurring in the shielding constant calculations.

two hydrogen atoms. This integral occurs with a small coefficient and is small in magnitude. For these reasons the charge density $\rho(h_i,h_j)$ was approximated by $\rho(h_i,h_j) = \frac{1}{2}S_1(h_i^2 + h_j^2)$. When integrated over all space the correct charge density and the approximate expression both yield S_1 . Thus the assumed density expression represents the same total amount of charge and places it in approximately the proper position. With this assumption

$P_X(h_i,h_j) = S_1 P_X(h_i,h_j)$ x appropriate component along

the X axis. An error of 0.01 in the value used for this integral in the best electrostatic density for ammonia, (0.0465) yields an error of 0.3% in the total electronic force. In water the value is 0.0570 which yields an error of 0.9% if it is out by 0.01 units.

PROGRAM 5.

Evaluation of three-centre force integrals.

The integrals were transformed to a polar co-ordinate system centred on the heavy nucleus. For example, for the force on H_1 perpendicular to the bond,

$$A = P(h_{2s}[\alpha], 2p_y[\beta]) = \int \frac{r^2 \sin^2\theta \cos^2\varphi \; e^{-power}}{[\rho^2 + r^2 - 2\rho r \cos\theta]^{3/2}}$$

$$B = P(h_{2s}[\alpha], 2s[\beta]) = \int \frac{r^2 \sin\theta \cos\varphi \; e^{-power}}{[\rho^2 + r^2 - 2\rho r \cos\theta]^{3/2}}$$

$$C = P(h_{2s}[\alpha], 2p_x[\beta]) = \int \frac{r^2 \sin\theta \cos\theta \cos\varphi \; e^{-power}}{[\rho^2 + r^2 - 2\rho r \cos\theta]^{3/2}}$$

$$Power = \beta r + \alpha[\rho^2 + r^2 - 2\rho r(\sin\theta \sin\varepsilon \cos\varphi + \cos\theta \cos\varepsilon)]^{1/2}$$

Here ρ is the bond length and θ is measured relative to X-H_1. The angle φ is measured from the H_1XH_2 plane. For the force along the X-H_1 bond, the numerators are slightly altered. The three centre potential energy integrals arising in the proton shielding constant calculations can be expressed in a similar notation.

In the machine program written by Miss O.Bosko, summation is first performed over increments of φ, followed

by a summation over increments of θ. For each 'shell' of constant r the numerical values of the integrals are punched out. Finally the calculation ceases automatically when the increments in one shell become less than a certain tolerance (1×10^{-6}). Convenient angular increments were found to be 20°. The small gain in accuracy achieved by using smaller increments was not justified by the great increase in computing time. With these increments the integration over one shell required 1½ minutes. Optimum radial increments were found to be 0.1 units, yielding a total computing time of 60-90 minutes for each set of input data. Typical results are shown in the following table for the force on a proton in ammonia.

DATA AND RESULTS FOR 3-CENTRE FORCE INTEGRAL. $P_{\parallel}(h, \phi_x)$

INPUT

$\zeta(h)=\alpha$	$\zeta(\phi_x)=\beta$	ρ	cosε	sinε
10000000 51	19500000 51	19160000 51	-28875000 50	95740000 50

$\Delta\psi$	$\Delta\theta$(radians)	$\Delta\phi$(radians)	tolerance
10000000 50	34906386 50	34906386 50	10000000 44

RESULTS

ΔA	ΔB	ΔC	A(total)	B(total)	C(total)	r
13189063 45	41626315 46	10576007 45	13189063 45	41626315 46	10576007 45	10000000 50
17198985 46	27313073 47	13835992 46	18517891 46	31475705 47	14893593 46	20000000 50
.....	.....	.....	.....	.....	.....	.....
66593745 43	10415857 44	-12204450 44	27357982 49	88857502 49	16265292 49	57000000 51
50173480 43	78904007 43	-93163203 43	27358032 49	88857581 49	16265199 49	58000000 51

A	A(normalized)	B	B (normalized)	C	C (normalized)	tolerance
27358032 49	46240392 49	88857581 49	86710266 49	16265199 49	27491348 49	10000000 44

ζ_i	ζ_x	a.u.	c°			
1.32	2.275	1.810	104.45	5514700049	8566900049	2508400049
1.32	2.275	1.810	109 28	5255400049	8316800049	1863100049
1.32	2.275	1.810	180		6856500049	-2340700049
1.29	1.950	1.905	107.3	5125900049	7535500049	1679500049
1.29	1.950	1.905	114	4768500049	7252400049	9287700048
1.29	1.950	1.905	120	4412200049	7027900049	3278800048
1.00	1.950	1.916	106 47	4624000049	8671000049	2749100049

ζ_i	ζ_x	a.u.	c°			
1.32	2.275	1.810		1150500050		
1.32	2.275	1.810	90	6118500049	3887400049	2414500049
1.32	2.275	1.810	104.45	4996200049	3006400049	1247300049
1.32	2.275	1.810	109 28	4644200049	2737500049	9436000048
1.00	2.275	1.810	120	4594800049	2162900049	7382500048
1.00	2.289	1.810	104.45	5458800049	2840200049	1466000049
1.29	1.950	1.905	107.3	4649400049	2835600049	1025600049
1.29	1.950	1.905	109 28	4495900049	2719100049	8983000048
1.29	1.950	1.905	114	4184600049	2483900049	6638000048
1.00	1.950	1.916	106 47	5125500049	2773600049	1287100049

(B) For homonuclear diatomic molecules.

In these expressions $Q = \zeta R$, C is Euler's constant and $E_i^*(x)$ is the exponential integral, defined by $E_i^*(x) = -E_i(-x) = \int_x^\infty (e^{-t}/t)dt$.

The formulae are taken from the lists of Coulson (71) where they are expressed in a different notation.

$$A(2s,2p_\sigma) = \frac{1}{R^2}\frac{Q^2}{3\sqrt{3}}$$

$$P(1s,1s) = \frac{1}{R^2}[1 - (1 + 2Q + 2Q^2)e^{-2Q}]$$

$$P(2s,2s) = \frac{1}{R^2}[1 - (1 + 2Q + 2Q^2 + \tfrac{4}{3}Q^3 + \tfrac{2}{3}Q^4)\, e^{-2Q}]$$

$$P(2p_\sigma,2p_\sigma) = \frac{1}{R^2}[1 + \frac{1}{Q^2}(9 - [9 + 18Q + 19Q^2 + 14Q^3 + 8Q^4 + 4Q^5 + 2Q^6]\, e^{-2Q})]$$

$$P(2p_\pi,2p_\pi) = \frac{1}{R^2}[1 - \frac{1}{2Q^2}(9 - [9 + 18Q + 16Q^2 + 8Q^3 + 2Q^4]\, e^{-2Q})]$$

$$P(2s,2p_\sigma) = \frac{1}{R^2}\frac{1}{\sqrt{3}Q}[5 - (5 + 10Q + 10Q^2 + 7Q^3 + 4Q^4 + 2Q^5)\, e^{-2Q}]$$

$$P(3d_\sigma, 3d_\sigma) = \frac{1}{R^2}\left[1 + \frac{12}{Q^2} + \frac{450}{Q^4} - \left(\frac{450}{Q^4} + \frac{900}{Q^3} + \frac{912}{Q^2} + \frac{624}{Q}\right.\right.$$
$$\left. + 325 + 138Q + 50Q^2 + 16Q^3 + \frac{40}{9}Q^4\right.$$
$$\left.\left. + \frac{4}{3}Q^5 + \frac{4}{9}Q^6\right) e^{-2Q}\right]$$

$$P(3d_\pi, 3d_\pi) = \frac{1}{R^2}\left[1 + \frac{6}{Q^2} - \frac{300}{Q^4} + \left(\frac{300}{Q^4} + \frac{600}{Q^3} - \frac{594}{Q^2} - \frac{194}{Q}\right.\right.$$
$$\left.\left. + 187 - 70Q + \frac{62}{3}Q^2 + \frac{14}{3}Q^3 + \frac{2}{3}Q^4\right) e^{-2Q}\right]$$

$$O(1s, 1s) = \frac{1}{R^2}\, 2\left[e^Q E_i^*[2Q](Q^2 - 3Q + 3)\right.$$
$$\left. + e^{-Q}(C + \ln 2Q)(Q^2 + 3Q + 3) - e^{-Q}(3Q^2 + 6Q)\right]$$

$$O(2s, 2s) = \frac{1}{R^2}\,\frac{2}{3}\left[e^Q E_i^*[2Q][Q^3 - 5Q^2 + 12Q - 12]\right.$$
$$-e^{-Q}[C + \ln 2Q][Q^3 + 5Q^2 + 12Q + 12]$$
$$\left. + e^{-Q}\left(\frac{1}{3}Q^4 + \frac{10}{3}Q^3 + 12Q^2 + 24Q\right)\right]$$

$$O(2p_\sigma, 2p_\sigma) = \frac{1}{R^2}\, 2\left[e^Q E_i^*[2Q]2(Q^3 - 9Q^2 + 45Q - 150 + \frac{315}{Q} - \frac{315}{Q^2})\right.$$
$$-e^{-Q}[C + \ln 2Q]\, 2(Q^3 + 9Q^2 + 45Q + 150 + \frac{315}{Q} + \frac{315}{Q^2})$$
$$\left. + e^{-Q}\left(\frac{1}{3}Q^4 + 8Q^3 + 55Q^2 + 250Q + 630 + \frac{1260}{Q}\right)\right]$$

$$O(2p_\pi, 2p_\pi) = \frac{1}{R^2}\, 2\left[e^{Q}\, E_i^{*}[2Q]\, 3\left(-Q^2 + 10Q - 45 + \frac{105}{Q} - \frac{105}{Q^2}\right)\right.$$

$$- e^{-Q}[C + \ln 2Q]\, 3\left(Q^2 + 10Q + 45 + \frac{105}{Q} + \frac{105}{Q^2}\right)$$

$$\left. + e^{-Q}\left(\frac{1}{3}Q^3 + \frac{25}{2}Q^2 + 95Q + 315 + \frac{630}{Q}\right)\right]$$

$$O(2s, 2p_\sigma) = \frac{1}{R^2}\,\frac{2}{\sqrt{3}}\left[e^{Q}\, E_i^{*}[2Q]\left(-Q^3 + 5Q^2 - 15Q + 30 - \frac{30}{Q}\right)\right.$$

$$-e^{-Q}\,[C + \ln 2Q]\left(Q^3 + 5Q^2 + 15Q + 30 + \frac{30}{Q}\right)$$

$$\left. + e^{-Q}\left(\frac{1}{3}Q^4 + \frac{19}{6}Q^3 + \frac{79}{6}Q^2 + 30Q + 60\right)\right]$$

$$O(2p_\sigma, 2s) = \frac{1}{R^2}\,\sqrt{3}\left[e^{Q}\, E_i^{*}[2Q]\, 4\left(-\frac{1}{3}Q^3 + 3Q^2 - 13Q + 30 - \frac{30}{Q}\right)\right.$$

$$-e^{-Q}\,[C + \ln 2Q]\, 4\left(\frac{1}{3}Q^3 + 3Q^2 + 13Q + 30 + \frac{30}{Q}\right)$$

$$\left. + e^{-Q}\left(\frac{2}{9}Q^4 + \frac{49}{9}Q^3 + \frac{337}{9}Q^2 + 120Q + 240\right)\right]$$

Overlap integrals.

$$S(1s, 1s) = \left(1 + Q + \frac{1}{3}Q^2\right) e^{-Q}$$

$$S(2s, 2s) = \left(1 + Q + \frac{4}{9}Q^2 + \frac{1}{9}Q^3 + \frac{1}{45}Q^4\right) e^{-Q}$$

$$S(2p_\sigma, 2p_\sigma) = \left(-1 - Q - \frac{1}{5}Q^2 + \frac{2}{15}Q^3 + \frac{1}{15}Q^4\right) e^{-Q}$$

$$S(2p_\pi, 2p_\pi) = \left(1 + Q + \frac{2}{5}Q^2 + \frac{1}{15}Q^3\right) e^{-Q}$$

$$S(2s, 2p_\sigma) = \frac{Q}{2\sqrt{3}}\left(1 + Q + \frac{7}{15}Q^2 + \frac{2}{15}Q^3\right) e^{-Q}$$

(C) For heteronuclear molecules.

In addition to Coulson's tables (71) some of these penetration integrals were evaluated by the method of Bader (69). For the sake of simplicity the Q values of the two participating atomic orbitals will be designated by α and β. Thus P(2s[α],2p[β]) has $\alpha = \zeta_{2s} R$ and $\beta = \zeta_{2p} R$. Furthermore, $X = \alpha + \beta$.

$$A(1s[\alpha], 2p_{\sigma}[\beta]) = \frac{1}{R^2} \cdot \frac{4\alpha^{3/2}\beta^{5/2}}{3X^2}$$

$$A(2s[\alpha], 2p_{\sigma}[\beta]) = \frac{1}{R^2} \cdot \frac{8\alpha^{5/2}\beta^{5/2}}{3\sqrt{3}X^3}$$

$$A(3d_{\delta}[\alpha], 2p_{\sigma}[\beta]) = \frac{1}{R^2} \cdot \frac{16\sqrt{2}\alpha^{7/2}\beta^{5/2}}{15X^4}$$

$$A(3d_{\pi}[\alpha], 2p_{\pi}[\beta]) = \frac{1}{R^2} \cdot \frac{8\sqrt{2}\alpha^{7/2}\beta^{5/2}}{5\sqrt{3}X^4}$$

$$P_{\parallel}(1s[\alpha], 2p_{\sigma}[\beta]) = \frac{1}{R^2} \cdot \frac{4\alpha^{3/2}\beta^{5/2}}{X^5} [16 - (16 + 16X + 8X^2 + 3X^3 + X^4) e^{-X}]$$

$$P_{\parallel}(1s[\alpha], 2s[\beta]) = \frac{1}{R^2} \cdot \frac{4\alpha^{3/2}\beta^{5/2}}{\sqrt{3}X^4} [6 - (6 + 6X + 3X^2 + X^3)e^{-X}]$$

$$P_{\pi}(2s[\alpha],2p_{\sigma}[\beta]) = \frac{1}{R^2}\cdot\frac{4a^{5/2}\beta^{5/2}}{\sqrt{3}\,X^6}\,[80 - (80 + 80X + 40X^2 + 14X^3 + 4X^4 + X^5)\,e^{-X}]$$

$$P_{\pi}(3d_{\delta}[\alpha],2p_{\sigma}[\beta]) = \frac{2^8\sqrt{2}\,a^{7/2}\beta^{5/2}}{R^2\,X^7}\,[1 + \frac{72}{X^2} - (\frac{72}{X^2} + \frac{72}{X} + 37 + 13X + \frac{7}{2}X^2 + \frac{37}{48}X^3 + \frac{7}{48}X^4 + \frac{5}{192}X^5 + \frac{1}{192}X^6)\,e^{-X}]$$

$$P_{\pi}(3d_{\pi}[\alpha],2p_{\pi}[\beta]) = \frac{768\,a^{7/2}\beta^{5/2}}{R^2\sqrt{6}\,X^7}\,[1 - \frac{48}{X^2} + (\frac{48}{X^2} + \frac{48}{X} + 23 + 7X + \frac{3}{2}X^2 + \frac{11}{48}X^3 + \frac{1}{48}X^4)e^{-X}]$$

$$P_{\pi}(3d_{\sigma}[\alpha],2s[\beta]) = \frac{8064\,a^{7/2}\beta^{5/2}}{R^2\sqrt{6}\,X^8}\,[1 - (1 + X + \frac{1}{2}X^2 + \frac{1}{6}X^3 + \frac{1}{24}X^4 + \frac{13}{1512}X^5 + \frac{5}{3024}X^6 + \frac{1}{3024}X^7)\,e^{-X}]$$

$$P_{\pi}(3d_{\sigma}[\alpha],1s[\beta]) = \frac{1152\,a^{7/2}\beta^{3/2}}{R^2\sqrt{2}\,X^7}\,[1 - (1 + X + \frac{1}{2}X^2 + \frac{1}{6}X^3 + \frac{1}{24}X^4 + \frac{1}{108}X^5 + \frac{1}{432}X^6)\,e^{-X}]$$

$$P_{\perp}(2s,2p_{\pi}) = \frac{1}{R^2}\cdot\frac{1}{\sqrt{3}Q}\left[\frac{5}{2} - \left(\frac{5}{2} + 5Q + 5Q^2 + 3Q^3 + Q^4\right) e^{-2Q}\right]$$

$$P_{\perp}(2p_{\sigma},2p_{\pi}) = \frac{1}{R^2}\cdot\frac{1}{Q^2}\left[\frac{9}{2} - \left(\frac{9}{2} + 9Q + 9Q^2 + 6Q^3 + 3Q^4 + Q^5\right)e^{-2Q}\right]$$

$$O_{ij}(1s[\alpha],1s[\beta]) = \frac{1}{R^2}\cdot\frac{2\alpha^{5/2}}{\beta^{5/2}} \times$$

$$\left[\begin{array}{l} \left[\left(3 - 3\beta + \beta^2\right) e^{\beta} E_i^{*}[\alpha+\beta]\right. \\ \\ \left. + \left(3 + 3\beta + \beta^2\right) e^{-\beta}\left(\log\frac{\alpha+\beta}{\alpha-\beta} - E_i^{*}[\alpha-\beta]\right)\right] \\ \\ + \dfrac{+2\beta}{\alpha(\alpha^2-\beta^2)}\cdot\begin{cases} -\left[(3\alpha^2 - 2\beta^2)(1+\beta) + \beta^2(\alpha^2-\beta^2)\right]e^{-\beta} \\ +\left[(3\alpha^2 - 2\beta^2 + \alpha\beta^2)e^{-\alpha}\right] \end{cases} \end{array}\right]$$

Note: If $\alpha<\beta$ in any overlap force expressions the transformation

$$\left[\log\frac{\alpha+\beta}{\alpha-\beta} - E_i^{*}[\alpha-\beta]\right] = \left[\log\frac{\alpha+\beta}{\beta-\alpha} + E_i[\beta-\alpha]\right]$$

can be employed, where $E_i(x) = \int_{-\infty}^{x} (e^t/t)dt$.

The remaining overlap force expressions are listed in terms of Coulson's analytical expressions (71) J_x. In some cases all or parts of the integrals have to be

evaluated by the method of Barnett and Coulson (68) in which case they are defined by $J_{(k,l,m)}$ in their notation. All normalizing factors are omitted in these formulae.

$$O_{\parallel}(2s[\alpha],1s[\beta]) = J_{34}$$

$$O_{\parallel}(2p_{\sigma}[\alpha],1s[\beta]) = J_{42}$$

$$O_{\parallel}(1s[\alpha],2s[\beta]) = J_{39}$$

$$O_{\parallel}(1s[\alpha],2p_{\sigma}[\beta]) = RJ_{33} - J_{42}$$

$$O_{\perp}(1s[\alpha],2p_{\pi}[\beta]) = J_{3} - J_{42}$$

$$O_{\parallel}(3d_{\sigma}[\alpha],1s[\beta]) = 3J_{3,1,1} - J_{1,1,1}$$

$$O_{\parallel}(1s[\alpha],3d_{\sigma}[\beta]) = 3R^2 J_{33} + 3J_{3,1,1} - 6R J_{42} - J_{40}$$

Overlap integrals.

One-centre:

$$S(1s[\alpha],2s[\beta]) = \frac{8\sqrt{3}\,\alpha^{3/2}\beta^{5/2}}{X^4}$$

Two-centre:

$$S(1s[\alpha],1s[\beta]) = \frac{8\,\alpha^{3/2}\beta^{3/2}}{[\alpha^2-\beta^2]^3}\,[\alpha([\alpha^2-\beta^2]-4\beta)\,e^{-\beta} + \beta([\alpha^2-\beta^2]+4\alpha)\,e^{-\alpha}]$$

$$S(1s[\alpha],2s[\beta]) = \frac{8\,\alpha^{3/2}\beta^{5/2}}{\sqrt{3}[\beta^2-\alpha^2]^4}\,[-([\beta^2-\alpha^2]^2 - 4[\beta^2-\alpha^2][\alpha+\beta^2] + 24\alpha\beta^2)\,e^{-\alpha} + (\alpha[\beta^2-\alpha^2]^2 + 4\alpha[\beta^2-\alpha^2][2\beta-1] + 24\alpha\beta^2)\,e^{-\beta}]$$

$$S(1s[\alpha],2p_\sigma[\beta]) = \frac{32\,\alpha^{5/2}\beta^{5/2}}{[\beta^2-\alpha^2]^4}\,[-\beta(6+6\alpha-[\beta^2-\alpha^2])\,e^{-\alpha} + (6\beta+6\beta^2+2\beta[\beta^2-\alpha^2]+\tfrac{1}{4}[\beta^2-\alpha^2]^2)e^{-\beta}]$$

$$S(1s[\alpha],3d_\sigma[\beta]) = 3J_{22} - J_{18}$$

$$S(2p[\alpha],2p[\beta]) = \frac{32\,\alpha^{5/2}\beta^{5/2}}{[\alpha^2-\beta^2]^5}\,[\alpha(96\beta[1+\beta]+48\beta^3-[11\beta^2+\alpha^2][\alpha^2-\beta^2] + \beta[\alpha^2-\beta^2]^2)\,e^{-\beta} - \beta(96\alpha[1+\alpha]+48\alpha^3 + [11\alpha^2+\beta^2][\alpha^2-\beta^2]+\alpha[\alpha^2-\beta^2]^2)\,e^{-\alpha}]$$

$$S(2p[\alpha],2s[\beta]) = \frac{8\,\alpha^{5/2}\beta^{5/2}}{\sqrt{3}[\alpha^2-\beta^2]^5}\,[4\alpha(6[\alpha^2+7\beta^2][1+\beta] - [\alpha^2+11\beta^2][\alpha^2-\beta^2]+\beta[\alpha^2-\beta^2]^2)\,e^{-\beta} - (24\alpha[\alpha^2+7\beta^2][1+\beta]+8\alpha[\alpha^2+5\beta^2][\alpha^2-\beta^2] + [\alpha^2+3\beta^2][\alpha^2-\beta^2]2)\,e^{-\alpha}]$$

IV. CALCULATION OF INTEGRALS FOR MOLECULAR PROPERTIES.

(A) Diamagnetic susceptibility.

One-centre:

$$\langle 1s\ r^2\ 1s\rangle = R^2 \cdot \frac{3}{Q^2}$$

$$\langle 2s\ r^2\ 2s\rangle = R^2 \cdot \frac{15}{2Q^2} = \langle 2p_\delta\ r^2\ 2p_\delta\rangle = \langle 2p_\pi\ r^2\ 2p_\pi\rangle$$

$$\langle 1s[\alpha]\ r^2\ 2s[\beta]\rangle = R^2 \cdot \frac{480\ \alpha^{3/2}\ \beta^{5/2}}{\sqrt{3}\ X^6}$$

Two-centre:

$$\langle h_i\ r^2\ h_i\rangle = R^2\ [1 + \frac{3}{Q^2}]$$

$$\langle 1s\ r^2\ h\rangle = J_{18}$$

$$\langle 2s\ r^2\ h\rangle = J_{27}$$

$$\langle 2p_\sigma\ r^2\ h\rangle = -\frac{\partial}{\partial\alpha} \cdot J_{20}$$

Three-centre:

$$\langle h_i\ r^2\ h_j\rangle = \rho^2\ S_1 + K_{27} - 2\rho \sin[\varepsilon/2]\ K_7$$

Results.

The exponents used are those for the electrostatic calculations unless otherwise specified. The integrals are $\langle \phi_\alpha \, r_x^2 \, \phi_\beta \rangle$ where r_x refers to the heavy nucleus.

ϕ_α, ϕ_β	NH_3	NH_3 (Duncan)	H_2O	HF
1s, 1s	0.0668300		0.0505988	0.0400643
2s, 2s	1.972387		1.449100	1.148803
$2p_\sigma$, $2p_\sigma$	1.972387		1.449100	1.052608
2p , 2p	1.972387		1.449100	1.203367
1s, 2s	0.0326436		0.0469238	0.0371288
1s, h	0.0157878	0.0179133	0.0138335	0.00783306
2s, h	1.55425	1.81752	1.18133	0.947107
$2p_\sigma$, h	1.62764	1.58434	1.20331	0.819443
h_i, h_i	5.473832	6.671056	4.997863	4.734745
hi, hj	0.885096	1.949896	0.912333	-

(B) Proton magnetic shielding constant.

The integrals are all referred to the proton as origin.

One-centre:

$\langle h | 1/r \; h \rangle = \frac{Q}{R}$

Two-centre:

$$\langle h[\alpha]\ 1/r\ 1s[\beta]\rangle = \frac{1}{R}\frac{4\,\alpha^{3/2}\beta^{3/2}}{(\beta^2-\alpha^2)^2}\left[\,2\beta e^{-\alpha} - (2\beta+\beta^2-\alpha^2)e^{-\beta}\,\right]$$

$$\langle h[\alpha]\ 1/r\ 2s[\beta]\rangle = \frac{1}{R}\frac{4\,\alpha^{3/2}\beta^{5/2}}{\sqrt{3}[\beta^2-\alpha^2]^3}\left[2[3\beta^2+\alpha^2]\,e^{-\alpha}\right.$$

$$-([\beta^2-\alpha^2]^2 - 2[1-2\beta][\beta^2-\alpha^2]$$

$$\left.+\,8\beta^2)\,e^{-\beta}\,\right]$$

$$\langle h[\alpha]\ 1/r\ 2p_\sigma[\beta]\rangle = \frac{1}{R}\frac{4\,\alpha^{3/2}\beta^{5/2}}{(\beta^2-\alpha^2)^3}\left[8\beta[1+\alpha]\,e^{-\alpha}\right.$$

$$\left.-\,(8\beta[1+\beta]+4\beta[\beta^2-\alpha^2]+[\beta^2-\alpha^2]^2)e^{-\beta}\right]$$

$$\langle 1s\ 1/r\ 1s\rangle = \frac{1}{R}\left[1-(1+Q)\,e^{-2Q}\,\right]$$

$$\langle 2s\ 1/r\ 2s\rangle = \frac{1}{R}\left[1-\left(1+\frac{3}{2}Q+Q^2+\frac{1}{3}Q^3\right)e^{-2Q}\,\right]$$

$$\langle 2p_\delta\ 1/r\ 2p_\sigma\rangle = \frac{1}{R}\left[1+\frac{3}{Q^2}-\frac{1}{Q^2}\left(3+6Q+7Q^2+\frac{11}{2}Q^2\right.\right.$$

$$\left.\left.+\,3Q^4+Q^5\right)e^{-2Q}\,\right]$$

$$\langle 1s[\alpha]\ 1/r\ 2s[\beta]\rangle = \frac{1}{R}\frac{4\,\alpha^{3/2}\beta^{5/2}}{\sqrt{3}\ X^4}\left[6-(6+4X+X^2)\,e^{-X}\,\right]$$

$$\langle 2p_\delta[\alpha]\ 1/r\ 2s[\beta]\rangle = \frac{1}{R}\frac{16\,\alpha^{5/2}\beta^{5/2}}{\sqrt{3}\ X^6}\left[10-\left(10+10X+5X^2\right.\right.$$

$$\left.\left.+\,\frac{3}{2}X^3+\frac{1}{4}X^4\right)e^{-X}\,\right]$$

$$\langle 2p_\sigma[\alpha]\ 1/r\ 1s[\beta]\rangle = \frac{1}{R}\cdot\frac{32\,\alpha^{5/2}\beta^{3/2}}{X^5}\left[1-\left(1+X+\frac{1}{2}X^2+\frac{1}{6}X^3\right)e^{-X}\right]$$

$$\langle 2p_\pi\ 1/r\ 2p_\pi\rangle = \frac{3}{2}\langle 2s\ 1/r\ 2s\rangle - \frac{1}{2}\langle 2p_\sigma\ 1/r\ 2p_\sigma\rangle$$

Results:

All orbital exponents are those used in the electrostatic calculations. The integrals are $\langle \phi_\alpha\ (1/r)_{h_i}\ \phi_\beta\rangle$.

ϕ_α,ϕ_β	NH_3	H_2O	HF
h_i,h_i	1.290000	1.320000	1.316300
1s,1s	0.524934	0.552486	0.577034
2s,2s	0.513265	0.545544	0.572328
$2p_\sigma,2p_\sigma$	0.603253	0.627982	0.647021
$2p_\pi,2p_\pi$	0.468271	0.504325	0.531290
2p,1s	0.0178545	0.0164973	0.0169663
2s,1s	0.117692	0.128976	0.134577
2p,2s	0.182937	0.182431	0.176672
h_j,h_j	0.325290	0.348611	-
h_i,1s	0.0327656	0.0305349	0.0293214
h_i,2s	0.408965	0.393866	0.382349
$h_i,2p_\sigma$	0.511490	0.476807	0.418932
h_i,h_j	0.122119	0.144346	-

ϕ_α, ϕ_β	NH_3	NH_3 (ζ =1.00)	H_2O
$h_j, 2p_\pi$	0.162646	0.148830	0.159474
$h_j, 2p_\sigma$	0.002493	0.025368	0.014922
$h_j, 2s$	0.204918	0.234694	0.210304

C. Dipole moment.

The operator Z = r cosθ in the dipole moment formulae $\langle \phi_\alpha \; Z \; \phi_\beta \rangle$ is along the axis defined by ϕ_α and ϕ_β. It refers to the heavy nucleus as origin. Numerical values of the integrals have been given with the force integrals previously.

$$\langle 2p[\alpha] \; Z \; 2s[\beta] \rangle = R.\frac{160}{\sqrt{3}} \frac{\alpha^{5/2}\beta^{5/2}}{X^6} = R \frac{5}{2\sqrt{3}Q} \quad \text{when } \alpha = \beta.$$

$$\langle 2p[\alpha] \; Z \; 1s[\beta] \rangle = R.\frac{32 \times \alpha^{5/2}\beta^{3/2}}{X^5}$$

$$\langle 2p_\pi[\alpha] \; Z \; 3d_\pi[\beta] \rangle = R.\frac{64\sqrt{6}\,\alpha^{5/2}\beta^{7/2}}{X^7}$$

$$\langle 2p_\sigma[\alpha] \; Z \; 3d_\sigma[\beta] \rangle = R.\frac{128\sqrt{2} \times \alpha^{5/2}\beta^{7/2}}{X^7}$$

$$\langle h_i \; Z \; h_i \rangle = R$$

$$\langle h_i[\alpha] \; Z \; 2p[\beta] \rangle = RS(h_i[\alpha], 2p[\beta]) - \frac{1}{\zeta_h} S(2p[\alpha], 2p[\beta])$$

$$\langle h_i[\alpha]\ Z\ 2s[\beta]\rangle = RS(h_i[\alpha],2s[\beta]) - \frac{1}{\zeta_h} S(2p[\alpha],2s[\beta])$$

$$\langle h_i[\alpha]\ Z\ 1s[\beta]\rangle = RS(h_i[\alpha],1s[\beta]) - \frac{1}{\zeta_h} S(2p[\alpha],1s[\beta])$$

$$\langle h_i[\alpha]\ Z\ 3d[\beta]\rangle = 3\,J_{3,4,1} - J_{1,4,1}$$

In the polyatomic molecules the perpendicular component of the dipole moment is not zero. If $Y = r_\beta \sin\theta_\beta \cos\phi$,

$$\langle h_i[\alpha]\ Y\ 2p_\pi[\beta]\rangle = -\frac{1}{2}\langle h_i[\alpha]\ Z\ 2p_\sigma[\beta]\rangle$$

$$+ \frac{4R\,\alpha^{3/2}\beta^{5/2}}{[\beta^2-\alpha^2]^5}\,[12\beta(-2\alpha[5\beta^2+3\alpha^2] + [\alpha^2+\beta^2][\beta^2-\alpha^2])\,e^{-\alpha}$$

$$+ \alpha(24\beta[5\beta^2+3\alpha^2] + 12[\alpha^2+5\beta^2][\beta^2-\alpha^2]$$

$$+ 12\beta[\beta^2-\alpha^2]^2 + [\beta^2-\alpha^2]^3)\,e^{-\beta}\,]$$

D. Quadrupole coupling constant.

The operator $q = [3\cos^2\theta - 1]/r^3$ is taken along the symmetry axis, but can be transformed readily to point along a bond axis, when it is denoted by q_β. The angle between the symmetry axis and a bond axis is γ.

The numerical values refer to ammonia, with the electrostatic orbital exponents and bond parameters. (The deuteron quadrupole coupling constant for HF was evaluated with the integrals kindly supplied by Professor M. Kaplus.)

One centre:

$\langle 2p_\sigma \, q \, 2p_\sigma \rangle = \frac{1}{R^3} \cdot \frac{4Q^3}{15} = 1.977300$

$\langle 2p_\pi \, q \, 2p_\pi \rangle = -\frac{1}{R^3} \cdot \frac{2Q^3}{15} = -0.988650$

Two centre:

$\langle h_i \, q \, h_i \rangle = (\cos^2\gamma - \frac{1}{2}\sin^2\gamma)\langle h_i \, q_\beta \, h_i \rangle = -0.0621845$

$\langle h_i \, q \, 2p_\sigma \rangle = (\cos^2\gamma - \frac{1}{2}\sin^2\gamma)\langle h_i \, q_\beta \, 2p_\sigma \rangle = -0.074167$

$\langle h_i \, q \, 2s \rangle = (\cos^2\gamma - \frac{1}{2}\sin^2\gamma)\langle h_i \, q_\beta \, 2s \rangle = -0.026707$

$\langle h_i \, q \, 1s \rangle \simeq S_1 \langle h_i \, q \, h_i \rangle = -0.012088$

$\langle h_{i[\alpha]} \, q \, 2p_{\pi[\beta]} \rangle = 3 \sin\gamma \cos\gamma \times [R \cdot O(1s[\beta], 1s[\alpha]) - J_{3,-1,1}] = 0.098568$

$\langle h_i \, q_\beta \, h_i \rangle = -\frac{8Q^3}{3R^3} e^{-2Q} + \frac{2}{R} P[h_i, h_i]$

$\langle h_i \, q_\beta \, 1s \rangle = 3J_{2,-2,1} - J_{0,-2,1}$

$\langle h_i \, q_\beta \, 2s \rangle = 3J_{2,-1,1} - J_{0,-1,1}$

$\langle h_i \, q_\beta \, 2p_\sigma \rangle = 3J_{2,-1,1} - J_{1,-1,1}$

$\langle h_i \, q \, 1s \rangle = (\cos^2\gamma - \frac{1}{2}\sin^2\gamma)\langle h_i \, q_b \, 1s \rangle = -0.017833$

V. CALCULATION OF DENSITIES

In order to calculate the spatial distribution of the densities in the three hydride molecules, the orbitals were all expressed in terms of polar co-ordinates about the central atom. Thus in ammonia, if the bond length is ρ and the angle between the symmetry axis and a bond axis is γ, the three proton co-ordinates r_1, r_2 and r_3 become

$$r_1 = [\rho^2 + r^2 - 2\rho r(\cos\theta \cos\gamma + \sin\theta \sin\gamma \cos\varphi)]^{1/2}$$

$$r_{2,3} = [\rho^2 + r^2 - 2\rho r(\cos\theta \cos\gamma - \tfrac{1}{2} \sin\theta \sin\gamma \cdot [\cos\varphi \pm \sqrt{3} \sin\varphi])]^{1/2}$$

where φ is measured from the plane passing through $H_{(1)}$ and the symmetry axis. The procedure is therefore to read in the orbital coefficients, bond parameters and orbital exponents and some chosen range of r, θ and φ values. The orbital contributions to the density and the final density is computed at each point defined by r, θ and φ. Lines of constant desntiy are obtained by interpolation between the computed values, and are plotted on polar graph paper.

Any desired plane can be examined by suitable choice of r, θ and φ. To obtain a plane such as that shown for ammonia in the lower half of Figure 17, it is necessary to calculate manually the r values required for a range of θ values, or vice versa. Because of the symmetry of the systems considered, φ need never be increased beyond 60°. Increments of 10° for θ and 0.1 a.u. for r were adequate for most ranges, although smaller increments were required in the regions where the density changed rapidly.

The orbital coefficients for the best electrostatic densities are given here in terms of their respective co-ordinate systems.

Hydrogen fluoride.

ψ_o = 0.999304 1s - 0.0075187 s' + 0.0695626 p

ψ_b = -0.013866 1s - 0.315884 s' + 0.747854 p + 0.481459 h

ψ_1 = -0.238521 1s + 1.022725 s' + 0.104528 p

The density used for the density contour map was one at $\varepsilon_1 = 0°$:

ψ_o = 1s

ψ_b = -0.219485 s + 0.752239 p + 0.485551 h

ψ_1 = s

Water:

$$\nu_o = 1s$$

$$\nu_b = -0.109490\ s - 0.633912\ p_{x'} \pm 0.358651\ p_{y'} + 0.486474\ h_i - 0.243237\ h_j$$

$$\nu_1 = 0.999997\ s + 0.002566\ p_{x'}$$

Ammonia:

$$\nu_o = 1s$$

$$\nu_{b1} = -0.107356\ s + 0.531916\ p_Z + 0.444341\ p_X + 0.510448\ h_1 - 0.142925\ (h_2+h_3)$$

$$\nu_{b2} = -0.107356\ s + 0.531916\ p_Z - 0.222171\ p_X + 0.384811\ p_Y + 0.510448\ h_2 - 0.142925\ (h_1+h_3)$$

$$\nu_{b3} = -0.107356\ s + 0.531916\ p_Z - 0.222171\ p_X - 0.384811\ p_Y + 0.510448\ h_3 - 0.142925\ (h_1+h_2)$$

$$\nu_1 = 0.999994\ s - 0.003489\ p_Z$$

CLAIMS TO ORIGINAL RESEARCH

1. An investigation has been performed into the nature of binding in homonuclear diatomic molecules by using the Hellmann-Feynman theorem to calculate the forces exerted by electrons in specific molecular orbitals on the nuclei.
2. A similar investigation was made of hydride molecules possessing lone pairs of electrons.
3. A new method of determining the electron density distributions in molecules of known nuclear structure was developed. It was required that the electron density exert forces on the nuclei of the ammonia, water and hydrogen fluoride molecules equal and opposite to the forces due to the other nuclei. The resulting molecular systems were in electrostatic equilibrium.
4. A calculation of molecular properties determined by the one-electron density demonstrated that the predicted densities were capable of reproducing the measured values to within the experimental error. An elucidation of the relationship of these properties to distinct features of the density distributions was achieved.

5. Reasons were advanced to support the thesis that all hydride molecules with at least one lone pair of electrons in a single orbital have similar electronic structures to the three molecules studied in detail.

6. Density contour diagrams were presented which illustrated the important features of the predicted density distributions.

7. Berlin's definition of binding regions in diatomic molecules was extended to include polyatomic molecules. A new graphical method, which can be readily applied to different nuclei, was developed to obtain the binding regions in molecules.

8. Evidence was presented that these binding regions have a physical significance, since the predicted electronic structures have their maximum concentration of density in the regions which are binding with respect to the nuclear frameworks.

FUTURE APPLICATIONS.

The present work has shown that any change in the electron distribution of isolated hydride molecules which removes density from the strongly binding region between all of the nuclei leads to a breakdown of electrostatic equilibrium in the molecules. For this reason no lone pair hybridization can occur away from the protons and the bond orbitals in the polyatomic molecules cannot be localized along the bond axes.

While only the hydride molecules have been examined, the same principle of maximum binding almost certainly applies to other molecules as well. This implies that lone pair hybridization is not important in isolated molecules. Many theories of molecular structure have stressed the importance of lone pair interactions because of a correlation of hybridization with the nuclear framework. The present results indicate that a fruitful approach to problems of molecular structure will be one in which the lone pair electrons are considered to be undisturbed by bond formation. The bond electron density may then be concentrated where it can most efficiently bind the nuclei. An investigation of the Berlin binding regions for different ratios of nuclear charge will indicate where this binding region lies. Such an approach to molecular geometry will have the advantage of a firm theoretical foundation.

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