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The Physical Nature of the Lone Pair

I. Approaches to the Problem

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Despite the large number of experimental and theoretical studies on the size, shape, and orientation of lone pairs and their resulting stereochemical character, lone pairs still remain poorly defined in terms of quantitative observable properties of a molecule. Using the conformation of saturated molecules and barriers to internal rotation, experimental chemists have arrived at conflicting sizes and orientations for lone pairs. Most theoretical attempts to define lone pair properties have centered on such non-observables as localized molecular orbitals or have been based on studies on isolated molecules.

The use of observable properties to construct a consistent set of physical models to analyze the physical nature of lone pairs is discussed. Much as one probes an electric field with a test charge, probes such as H^+, H^-, He and H could be used to probe regions of molecules such as NH_3 and H_2O where lone pairs are often postulated to exist. *Ab initio* quantum mechanical studies can be analyzed using electron density (and resulting changes during interaction), total pair density of electrons, the electrostatic potential about the molecule and bond energy analysis to study lone pair properties. A simple study of NH_3 using an H^+ probe is presented to clarify the approach.

Key word: Lone pairs, physical nature of ~

1. Introduction

The physical nature of lone pairs of electrons is still a matter of investigation, largely because of the complexities of identifying and extracting their properties from the solutions to molecular quantum mechanical problems or from the results of experimental studies. Despite the large number of experimental and theoretical studies, conflicting conclusions about the size, shape, orientation and resulting stereochemical manifestations of lone pairs appear regularly in the chemical literature. Partly this is due to differences in experimental and theoretical approaches, but largely it is a result of considering only certain characteristics of lone pairs or approaching the problem through the use of non-observables.

Characteristics of a lone pair are, of course, not properties of a single pair of electrons, but of the entire electronic structure of the molecule. The usefulness of molecular orbitals as a basis for determining lone pair properties is therefore limited; in addition, molecular orbitals are non-observables. Studying lone pair interactions in large molecules by investigating the energies of many conformers leads to ambiguous results, as it is difficult to identify which changes in energy are due to lone pair properties and which are due to other electronic and geometric properties of the conformers [1–4]. Even when lone pairs are studied in isolated simple molecules like water or ammonia, the resulting electron density maps, while an observable of the system, do not adequately reflect how the lone pairs will be altered when intermolecular interactions occur.

In attempting to develop a comprehensive method for defining lone pair properties, certain features must be included.

1. It should be based on quantities which are observable in principle at least; the energy and its dissection and the total molecular electron density are examples of such properties.
2. It should be independent of the particular formalism in which the molecular wavefunctions are expressed; basically it should be basis set independent.
3. The mathematical statements used should provide a consistent set of physical models useful in interpreting the results of the analysis; in particular the stereochemical properties of lone pairs must be reflected in the analysis.

Since it is only in interaction with other atoms or molecules that lone pairs demonstrate their directionality and extent in space in a chemical sense, the suggestion is made here that lone pairs be probed with test species much in the same way that electrical fields are probed with test charges. The resulting energy surfaces and wavefunctions could be analysed in a consistent manner to make comparisons between molecules more useful. A simple approach to lone pair interactions with a He test species has been reported [5].

Test species representing open and closed shell atoms and ions (H^-, H, H^+, He) could be used as probes to study lone pairs in water, ammonia, phosphine and hydrogen sulfide. As the probe species is moved about the molecule, the molecular geometry will remain fixed to guarantee that changes which occur will be due to perturbations caused by the probe alone.

In addition to energy surfaces the following quantities and approaches would be useful in the interpretation and definition of lone pair properties:

1. electron density and density changes during interactions;
2. total pair density of electrons [6];
3. the electrostatic potential produced around the molecule [7];
4. bond energy analyses [8].

Electron density plots would be useful in identifying regions about a molecule rich in electron density but not associated with nuclei or bonds. Electron density gradients in these regions and how the regions vary upon probing with test species will help define the polarizability of the charge distribution. These variations would be closely related to the directionality of the lone pairs and how hard or soft they are. Analyses of this type, which are closely related to classical electrostatic arguments, are strengthened by the success of several classical lone pair models [9–11].

A study of the total pair density, and how it varies as the molecule is probed with test species, would provide information on the probability of an electron pair being closely associated with a given region of space about a molecule. This would give a measure of just how closely a single pair of electrons can be associated with a region of electron density. The rationale for studying the electrostatic potential about a molecule is that it includes the contributions from nuclear charges to the molecular field in a well defined way and would prove useful in identifying regions of total net non-zero potential away from nuclei and bonds.

Bond energy analysis has proven most useful in studying the structure of molecular complexes [12]. The total Hartree-Fock molecular energy is decomposed into one-, two-, three-, and four-center contributions and would provide an additional approach to study interaction between the test probes and the simple molecules.

Using the properties discussed above, a lone pair might be described as a region of space rich in electron density not associated with a nucleus or bond, which also has a high electron pair density and which is well-defined for neutral and charged probes; the information from the bond energy analysis will also be incorporated, as will the molecular electrostatic potential field.

The simple example of this approach to lone pair characterization presented in the next section was obtained within the Hartree-Fock framework; electron correlation of course is not completely accounted for with this method. None the less, there are many cases where the Hartree-Fock approach has proven most useful and very accurate in describing molecules with lone pairs. The inversion barrier in NH_3 [13], the rotation barriers of H_2O_2 [14, 15] and the bending frequency of C_3 [15] are examples of isolated molecular systems which are described by Hartree-Fock wave functions.

2. A Simple Example: NH_3+H^+

Unlike many of the NH_4^+ studies in the literature, which concentrate on H^+ approaching NH_3 along the C_3 axis [12, 16, 17], this lone pair study involves looking at the approach of H^+ to NH_3 along seventeen directions. The potential surface about the nitrogen in the region generally described as the lone pair was generated and the wavefunctions were analyzed for atomic charges and bonding effectiveness to the H^+ probe for the various approaches. Considering a large number of approaches of the probe provides a picture of the lone pair as it would appear in larger molecules where the steric nature of the lone pair is felt in directions other than along the C_3 axis.

The energy surface was generated using an ammonia molecule with N–H = 1.915 bohr and H–N–H angle = 106.77°. The ammonia geometry was held fixed as an H^+ probe was brought up to the molecule. The parameters defining the energy surface are shown in Fig. 1. The N–H^+ distance is R and the angles α and ϕ along with R denote the position of H^+ relative to the axis system shown in the figure. The set of angles $(\alpha, \phi)=(180°, 0°)$ is the C_3 symmetry axis approach of H^+, $(\alpha, \phi)=(90°, 0°)$ is an H^+ approach perpendicular to the C_3 axis, passing over an ammonia hydrogen. The set $(\alpha, \phi)=(90°, 60°)$ is an approach perpendicular to the C_3 axis and passing halfway between two hydrogens. Note α' in Fig. 1 is equal to $180°-\alpha$ where α is used in the Tables and other Figures.

A variety of basis sets was explored in generating the energy surface, including sets with polarization functions on nitrogen and hydrogen. The STO-3G [18] and 4-31G [19] basis sets were used initially. The Dunning Gaussian basis set [20,21], $(9s/5p)$ set contracted to $(5s/3p)$ on oxygen and $(4s)$ to $(3s)$ on hydrogen,

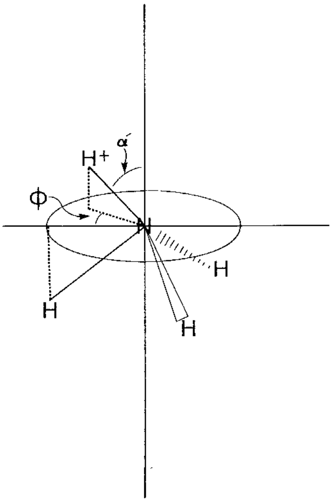

Fig. 1. Parameters Defining the Potential Energy Surface for $NH_3 + H^+$. Note α is $180 - \alpha'$

was used for the bulk of the results here. While the STO-3G and 4-31G basis sets gave results qualitatively similar to the Dunning basis set, finer detail in the surface was found with the latter. In addition the effects of polarization functions on nitrogen and hydrogen were explored. The Dunning basis set was augmented with polarization functions on nitrogen (six *d*-orbitals with $\rho = 2.0$) and on hydrogen (three *p*-orbitals, $\rho = 1.0$); the effects of these orbitals were investigated separately and together. Using these polarization functions, portions of the energy surface were recalculated and the minimum energy distances of approach were the same as with the Dunning set alone; changes in electronic charge on atoms and overlap population which are to be expected were observed, but followed similar trends to those observed with the unaugmented basis set. On the basis of these results, the Dunning basis set was used for the remainder of the calculations.

Table 1. Summary of potential energy surface of $NH_3 + H^+$ using the Dunning basis set

α	ϕ	0°	20°	40°	60°
75°	$-E^a$	56.2474	56.2507	56.2678	56.2779
	R^a	3.5	3.2	2.4	2.2
90°	$-E$	56.2564	56.2663	56.2937	56.3003
	R	3.1	2.8	2.2	2.1
120°	$-E$	56.3937	56.3973	56.4029	56.4052
	R	2.0	2.0	2.0	2.0
150°	$-E$	56.4931	56.4936	56.4947	56.4952
	R	1.9	1.9	1.9	1.9
180°	$-E$	56.5269			
	R	1.9			

[a] Minimum Energy for a given approach in atomic units, R of that energy in bohr.

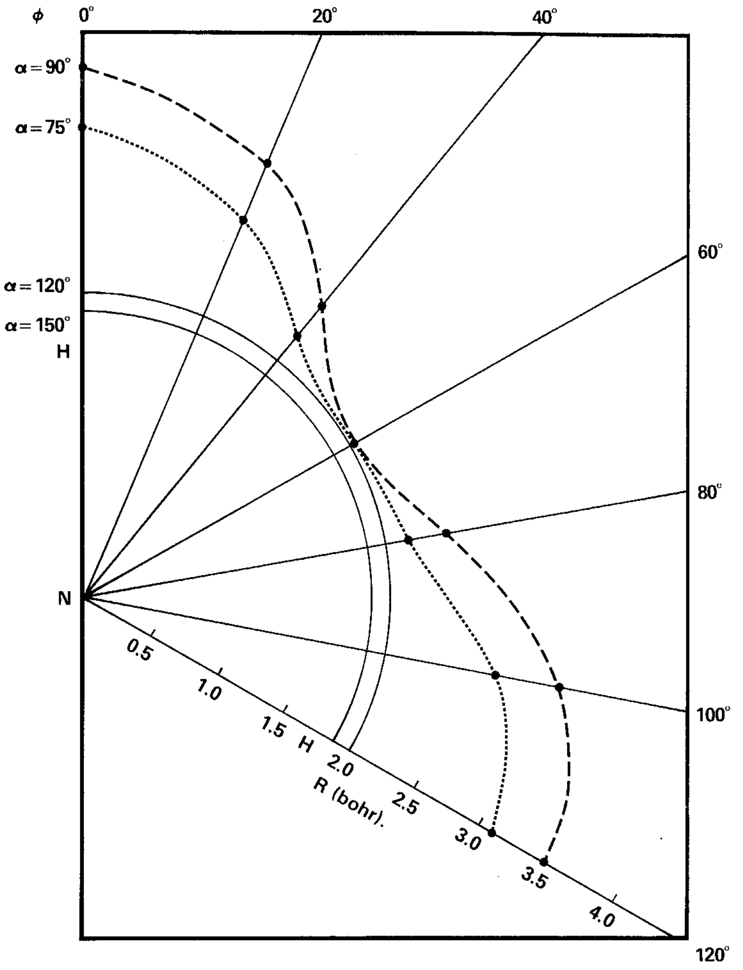

Fig. 2. Contours of Minimum Energy Distances for the Approach of H^+ to NH_3 Looking Down the C_3 Axis of NH_3. Dunning Basis Set

The potential energy surface for $NH_3 + H^+$ using the Dunning basis set is summarized in Table 1 and Figs. 2 and 3. The energies in Table 1 were obtained by moving the H^+ probe in toward the nitrogen atom with the ammonia molecule not being allowed to relax; the set of curves shown in Fig. 4 are typical of the manner in which the minimum energy and corresponding distance were determined. The further from the standard C_3 approach of H^+, the higher the energy, but each approach exhibited a minimum energy distance. Fig. 2 shows the distances of minimum energy for the seventeen approaches, plotted from a view looking down the C_3 axis of ammonia. The lone pair appears to be spherical with a radius of 2 bohr down to $\alpha = 120°$ and then expands into a three-leaf-clover configuration at $\alpha = 90°$ and 75° with minimum energy distances up to 3.5 bohr for the $(\alpha, \phi) = (75°, 0°)$ approach.

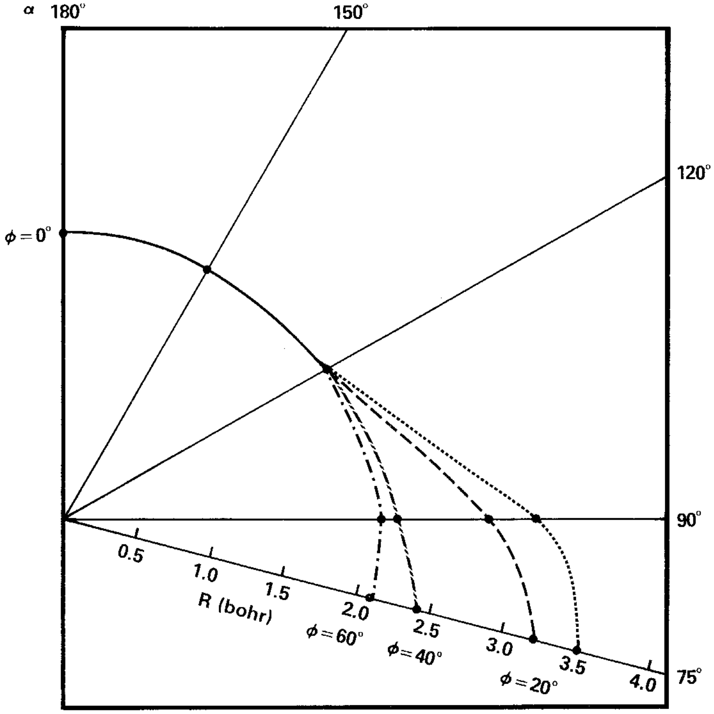

Fig. 3. Contours of Minimum Energy Distances for the Approach of H^+ to NH_3 Looking Perpendicular to the C_3 Axis of NH_3. Dunning Basis Set

A different view of the lone pair is seen in Fig. 3. There a side-on picture is presented, viewed from a perpendicular to the C_3 axis. For $\phi=60°$ and 40°, the lone pair is nearly spherical with a radius of about 2 bohr. For $\phi=0°$ and 20°, there is a considerable bulge in the sphere covering the three-leaf-clover base of the lone pair at $\phi=75°$.

Figs. 1 and 2 provide a picture of the "lone-pair" region of the molecule: a bell shape, spherical at the top and three-leaf-clover shape at the bottom. What remains to be seen is the magnitude of the interaction between the probe and the molecule; this will be discussed in terms of changes in electronic charge on atoms and the probe, and the overlap populations.

A review of overlap populations between the H^+ probe and the ammonia molecule shows fairly constant total positive overlap; the range is 0.27e at (75°, 0°) to 0.31e at (180°, 0°). For $\alpha=75°$ and 90°, the positive overlap population is a mixture of contributions from the N–H^+ (probe) population and the H–H^+ (probe) population, the latter H being the one or ones (at 60°) closest to the approaching probe. These overlap populations indicate that regardless of approach similar bonding magnitude exists between the probe and ammonia. Larger changes are seen in the total nitrogen-hydrogen overlap population which varies from 0.67e at (75°, 0°) to 1.01e in the isolated molecule.

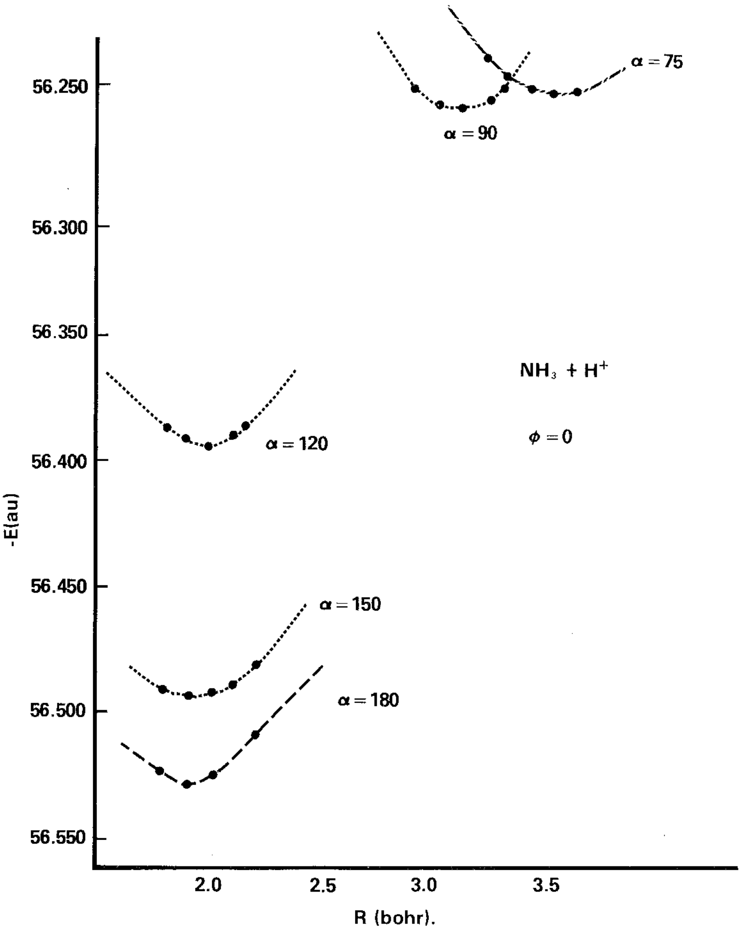

Fig. 4. Typical Energy Curves Used in the Determination of Minimum Energy Distances. Dunning Basis Set

Shifts in electronic charge on the atoms can also be analyzed. The charge on the H^+ varies from 0.37e at (75°, 0°) to 0.54e at (180°, 0°). On nitrogen this variation is 7.42e at (75°, 0°) and 7.82e at (180°, 0°) compared to 7.86e in the isolated molecule. For the three hydrogens in ammonia, the total electronic charge varies from 2.21e at (75°, 0°) to 1.64e at (180°, 0°) compared with 2.13e in the isolated molecule. With the approach of the H^+ probe, electronic charge is pushed onto the ammonia hydrogens, and pulled to the H^+, weakening the N–H intermolecular bonds. The net effect is to produce the N–H^+ probe interaction.

3. Conclusion

The general approach described here, and applied in part to the ammonia molecule, offers a systematic approach to determining "lone pair" properties under a variety of environmental interactions.

In polyatomic molecules where there is intramolecular interaction with the nitrogen lone pair, the interaction will not always occur along the C_3 axis of tetrahedral nitrogen. Hence, the interacting group may not be able to approach the lowest energy portions of the potential surface, but will be forced to approach in a less energetically favored direction where it will find a minimum energy for that approach. With this technique for defining shape, size and orientation, a bell shaped "lone pair" is found.

It is hoped that further studies using the approach will be undertaken.

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