The Lone-pair Orbital in NH_3 and the Calculation of the HNH Angle

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Summary A study has been made, using the Frost FSGO method, of the effect of modifying the form of the lone-pair orbital of NH_3 with a view to obtaining an improvement in the calculated value for the inter-bond angle, which is very low when the simple Frost method is used.

CALCULATIONS by Frost *et al.*[1] have shown that the simplest Floating Spherical Gaussian Orbital (FSGO) method gives very good values for the shapes of hydrocarbon molecules. These contain no lone-pairs. These results have been confirmed by Blustin.[2] However, the angles calculated for molecules such as CH_2, OH_2, and NH_3, which contain lone pairs, are very poor.[3] Here we present the results of some calculations designed to examine what modifications of the lone-pair orbital in NH_3 is required in order that the calculated inter-bond angle shall agree with experiment.

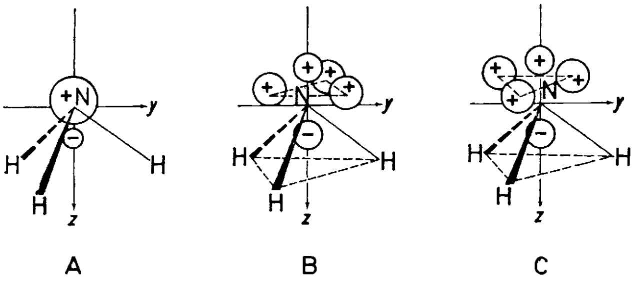

FIGURE. *Diagram (not to scale) of the combination of Gaussians tested as representations of the lone-pair orbital.*

The NH_3 molecule contains five electron pairs which occupy an inner-shell orbital, three bonding orbitals, and a lone-pair orbital. In the simple FSGO model each orbital is represented by a single Gaussian function, the radius and position being allowed to float to minimise the energy. In the modifications studied a linear combination of several spherical floating Gaussian functions is used to represent the lone-pair orbital, single Gaussians being retained for the other orbitals:

$$\phi\,(\text{lone-pair}) = N \sum_j C_j \left(\frac{2}{\pi\rho_j^2}\right)^{3/4} \exp\,[-(\underline{r} - \underline{R}_j)^2/\rho_j^2]$$

where r is the electronic radial-co-ordinate, ρ_j is the 'radius' of the jth Gaussian orbital, $\underline{R}_j$ the location of the 'centre' of the Gaussian; N is the normalisation constant and the C_js linear coefficients which can be positive or negative.

TABLE

Model	Simple FSGO	A[d]	B[d]	C[d]
E(Hartrees) ..	−47·568	−47·704	−47·944	−47·953
∠HNH (106·7°)[c]	87·9°	93·2°	100·4°	106·3°
rNH (a.u.) (1·91)[c]	1·91	1·90	1·91	1·90
Inner shell orbital				
ρ (a.u.) ..	0·277	0·278	0·278	0·278
z (a.u.)	0·001	0·001	0·002	0·001
Bonding orbital ..				
ρ (a.u.) ..	1·551	1·528	1·566	1·543
d[a] (a.u.) ..	0·80	0·84	0·88	0·92
θ[b]	83·4°	90·3°	98·9°	106·8°
Lone pair orbital axial positive lobe				
ρ	1·625	1·561	0·687	0·682
z	0·147	−0·012	−0·176	−0·156
c	1·0	1·0	0·775	0·682
Axial negative lobe				
ρ		0·596	0·638	0·648
z		0·461	0·187	0·168
c		−0·067	−0·720	−0·651
Outer positive lobe				
ρ			1·625	1·585
y			−0·524	0·714
z			−0·145	−0·104
c			1·0	1·0

[a] d Is the distance of the bonding pair from the nitrogen atom.
[b] θ Is the angle made by the bonding pairs with the N atom.
[c] The figures in brackets are the experimental values.
[d] See Figure.

The three modifications examined are illustrated in the Figure. In A the orbital has two axial Gaussian lobes, one positive and one negative. In B it has, in addition, three equivalent off-axis Gaussians which are staggered with respect to the NH bonds, whereas in C these are eclipsed. The results are listed in the Table.

These results show that, with a lone-pair orbital constructed as in C a good value for the angle is calculated. This success is achieved without adding complexity to the other orbitals which are throughout represented by single

Gaussian functions. Moreover, the value for the calculated NH bond length remains good. The other orbitals vary very little except as regards the angular distribution of the bonding orbitals. Calculations using seven other combinations of Gaussians for the lone-pair orbital which are related to those included in the Table were performed. These showed that the full combination used in C is required to give the correct angle.

The final lone-pair orbital C is spread more widely round the nitrogen atom than one formed from a single Gaussian. This feature appears to be a requisite as also does the inclusion of a negative lobe. Also, if the axial positive Gaussian is omitted from C, agreement is lost. It is interesting that an eclipsed trio of Gaussian functions is preferred to a staggered set. A full understanding of this would require a much more detailed study of the importance, and variation, of overlap and of the exact charge distribution. It is to be noted also (i) that model C (eclipsed) provides a lower energy than model B (staggered), and (ii) that the two axial lobes alone correspond well to an antisymmetric *p*-orbital.

Similar conclusions have been reached for CH_2 (lowest singlet). A similar combination of Gaussians (*i.e.* two axial Gaussians forming an antisymmetric *p*-orbital together with two equivalent off-axis Gaussians eclipsed to the CH bonds) is required to give a good calculated angle (calc. 103·5°, obs. 102·4°).

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[2] P. H. Blustin, Ph.D. Thesis, Cambridge, 1972.

[3] A. A. Frost, *J. Phys. Chem.*, 1968, **72**, 1289.