Ionic Character and Hybridization of Ammonia Molecule

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Townes and Dailey[1] have determined the electronic structure of molecules from the nuclear quadrupole coupling constants. In the present paper, this theory has been applied to the ammonia molecule. On the basis of the theoretical results, together with the experimental value of the dipole moment, some discussion has been made on the ionic character of the N-H bond and the *s*–*p* hybridization of the nitrogen atom. The following VB function has been assumed to the ground state of the molecule,

$$\Psi_T = A\,[\Psi_{\text{cov}} + 3\lambda\Psi_{\text{ion}1} + 3\lambda^2\Psi_{\text{ion}2} + \lambda^3\Psi_{\text{ion}3}] \quad (1)$$

Here A represents the normalization factor, the coefficient λ is concerned with the magnitude of the ionic character of the N-H bond and the wavefunctions $\Psi_{\text{ion}1}$, $\Psi_{\text{ion}2}$, and $\Psi_{\text{ion}3}$ respectively refer to the singly, doubly and triply ionized structure. To each configuration the following electron pair bond functions are assumed:

$$\left.\begin{aligned}\Psi_{\text{cov}} &= (N_l)^2(N_1H_1)^2(N_2H_2)^2(N_3H_3)^2\\ \Psi_{\text{ion}1} &= (N_l)^2(N_1)^2(N_2H_2)^2(N_3H_3)^2\\ \Psi_{\text{ion}2} &= (N_l)^2(N_1)^2(N_2)^2(N_3H_3)^2\\ \Psi_{\text{ion}3} &= (N_l)^2(N_1)^2(N_2)^2(N_3)^2\end{aligned}\right\} \quad (2)$$

Here N_l and N_i (i=1, 2 and 3) are the lone pair orbital and the equivalent orbitals on the nitrogen atom and $(N_iH_i)^2$ is the normalized bond orbital of the Heitler-London type. When the structure of the ammonia molecule is considered to belong to the symmetry species C_{3v}, N_l and N_i orbitals are expressed as follows:

$$\left.\begin{aligned}H_l &= \alpha S + \sqrt{3}\,\beta P_z\\ N_1 &= \gamma S + \sqrt{\tfrac{1}{6}}\delta P_x + \sqrt{\tfrac{1}{2}}\delta P_y + \sqrt{\tfrac{1}{3}}\varepsilon P_z\\ N_2 &= \gamma S + \sqrt{\tfrac{1}{6}}\delta P_x - \sqrt{\tfrac{1}{2}}\delta P_y + \sqrt{\tfrac{1}{3}}\varepsilon P_z\\ N_3 &= \gamma S - \sqrt{\tfrac{2}{3}}\delta P_x + \sqrt{\tfrac{1}{3}}\varepsilon P_z\end{aligned}\right\} \quad (3)$$

Here S, P_x, P_y and P_z represent the Slater AO's and the coordinate system was taken as shown in Fig. 1. By considering the orthonormalization conditions for Eq. 3, the number of coefficients to be determined is reduced to only one ε.

The dipole moment and the quadrupole coupling constant are expressed as follows:

$$\mu = e\Big(\sum_{i=1}^{3} r_i - \sum_{j=1}^{8}\overline{Z}_j\Big),\quad \overline{Z}_j = \int|\Psi_T|^2 Z_j\,dv \quad (4)$$

$$eQq = -e^2Q\int|\Psi_T|^2(3\cos^2\theta_z - 1)r^{-3}dv \quad (5)$$

$$\approx eQq_{pz}f(\lambda, \varepsilon) \quad (5')$$

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[1] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

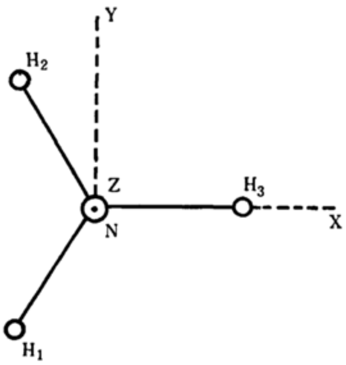

Fig. 1. The coordinate system of NH_3 molecule. Length N–H=1.014 Å. Angle H_i–N–H_j=106° 47′ 11).

$$q_{pz}=-e\int|\Psi_{n:2pz}|^2(3\cos^2\theta_z-1)r^{-3}\mathrm{d}v \qquad (6)$$

(e: protonic charge, 4.802×10^{-10} e.s.u.)

We followed the theory of Townes and Dailey that the contribution to the field gradient at the nitrogen nucleus depends exclusively upon the p electrons of the nitrogen atom. Moreover, since we have had no experimental value for eQq_{pz} of the nitrogen atom, we used a value −11.12 *Mc.* calculated with the aid of the $2pz$ SCF AO of the ground state ^4S of the nitrogen atom, which was obtained to fit to Hartree-Fock field by Hartree and Hartree2). We used the microwave data for the experimental values, $\mu=1.468\,D$ and $eQq=-4.0842$ *Mc.*3), and all the overlap integrals and the dipole moment matrix integrals were evaluated by the ordinary method4). These values are tabulated in Table I.

TABLE I. OVERLAP INTEGRAL: $S_{ab}=\int\chi_a\chi_b\mathrm{d}v$

DIPOLE MOMENT MATRIX INTEGRAL:

$M_{ab}=\int\chi_a Z\chi_b\mathrm{d}v$ (in *a.u.*).

The following abbreviated notations for AO's are used: h_i=(H: 1s), s=(N: 2s), x=(N: 2px), y=(N: 2py) and z=(N: 2pz).

S_{h_is}	0.510836	$M_{h_ih_i}$	0.718747
S_{h_iz}	0.151483	M_{h_is}	0.168502
S_{h_1x}	−0.187118	M_{h_iz}	0.461132
S_{h_2x}	−0.187118	M_{sz}	0.0866768
S_{h_3x}	0.374235	M_{h_1x}	0.0640552
		M_{h_2x}	0.0640552
		M_{h_3x}	0.128110
		M_{h_1y}	0.111230
		M_{h_2y}	0.111230
		M_{h_3y}	0

The parameters ε and λ were determined as 0.9465 and −0.38, respectively, by the aid of Eqs. 4 and 5′, and the observed values of μ and eQq. The normalized hybrid orbitals of the nitrogen atom then become,

$$\left.\begin{aligned}
N_l&=0.8395S-0.5434P_z\\
N_1&=0.3137S-0.4082P_x-0.7071P_y\\
&\quad+0.4847P_z\\
N_2&=0.3137S-0.4082P_x+0.7071P_y\\
&\quad+0.4847P_z\\
N_3&=0.3137S+0.8165P_x+0.4847P_z
\end{aligned}\right\}\qquad(2)$$

TABLE II. RELATIVE WEIGHTS OF VALENCE STRUCTURE IN NH_3 AND S CHARACTER OF THE HYBRID ORBITAL OF N ATOM

Structure		Weight of structure %	
		Present	Syrkin et al.
Covalent form	(I)	14.5	16
Single ionic form	(II)	18.8	13.5
Double ionic form	(III)	2.7	3.9
Triple ionic form	(IV)	0.1	0.3
Transitional	(I)—(II)	33.0	27.3
〃	(I)—(III)	12.5	15
〃	(I)—(IV)	1.6	3
〃	(II)—(III)	14.3	15
〃	(II)—(IV)	1.8	4
〃	(III)—(IV)	0.7	2

S character %

	Present	Duncan & Pople	Higuchi
For lone pair orb.	70.5	38.9	71.4
For equivalent orb. (each)	9.8	4.1	3.2

Thus we get the estimates of the ionic character and the s–p hybridization of NH_3 molecule. These are given in Table II, together with the estimated values by other authors. Several views for the orbitals of $NH_3$5–8) has been already reported, however we can not always compare those with the present results since those orbitals are almost described in

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2) D. R. Hartree and W. Hartree, *Proc. Roy. Soc.* (*London*), **A193**, 299 (1948). This result for $2pz$ function can be approximated in the following analytical form:

$$(3/4\pi)^{1/2}\cos\theta_z r[1.809\,e^{-1.387r}+6.620\,e^{-2.950r}]$$

We calculated q_{pz} by this function.

3) G. R. Gunther-Mohr, R. L. White and A. L. Schawlow, *Phys. Rev.*, **94**, 1184 (1954).

4) For example, M. Kotani et al., "Table of Molecular Integrals", Maruzen Co., Ltd., Tokyo (1955).

5) A. B. F. Duncan and J. A. Pople, *Trans. Faraday Soc.*, **49**, 217 (1953).

6) J. Higuchi, *J. Chem. Phys.*, **24**, 535 (1956).

7) H. Kaplan, ibid., **26**, 1704 (1957).

8) A. B. F. Duncan, ibid., **27**, 423 (1957).

MO and not in Heitler-London type. When we dare to compare, they have some differences from ours as above mentioned. Here Duncan and Pople's orbitals(5) are determined in such a way as the parameters in orbitals are well fitted to the experimental value of the dipole moment of NH_3, and Higuchi's ones(6) are obtained following Roothaan's SCF procedure(9), in which all the electrons in molecule take part in setting up MO, so that the orbitals are considered more accurate than the present and Duncan and Pople's ones. Also, Syrkin et al.(10) have estimated the ionic character of the structure from the base of the additivity of bond moment. On the other hand, our estimations are made taking into consideration the nuclear quadrupole coupling constant besides the dipole moment. However these both estimates may be said to be equal substantially.

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9) C. C. J. Roothaan, *Revs. Modern Phys.*, **23**, 69 (1951).

10) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond", Butterworths Scientific Publications, London (1950), p. 208.

11) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Co., Inc., New York (1945), p. 439.