

THE LOW LYING STATES OF AMMONIA; GENERALIZED VALENCE BOND AND CONFIGURATION INTERACTION STUDIES^{*}

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The nine lower singlet and triplet states of ammonia were studied using ab initio generalized valence bond (GVB) and configuration interaction (CI) wavefunctions. The eight lowest (vertical) excited states were found to be Rydberg in nature. Vertical excitation energies were determined to be (in eV): 6.14 and 6.37 for $n \rightarrow 3s$; 7.86 and 7.88 for $n \rightarrow 3p_{x,y}$, and 7.87 and 8.15 for $n \rightarrow 3p_z$ (in each case the triplet energy is first). These results are in excellent agreement (0.06 eV average error) with the observed electron impact excitation energies (in eV), 6.39 (A^1A_2''), 7.93 (B^1E''), and 8.26 (C^1A_1'). The small singlet–triplet energy splittings are consistent with those expected for Rydberg-like excited states. We find no vertical transition consistent with the small peak at 4.4 eV apparently observed in threshold electron impact experiments.

1. Introduction

The lower excited states of ammonia have been the object of experimental [1–4] and theoretical [5–8] investigations. Despite these studies the nature and location of low-lying triplet and singlet excited states are not completely understood [3,7,9,10]. In order to further elucidate the character of these transitions and in particular the triplet states, ab initio generalized valence bond (GVB) and configuration interaction (CI) calculations have been performed on the \tilde{X}^1A_1 , $\tilde{A}^3,1A_2''$, $\tilde{B}^3,1E''$, $\tilde{C}^3,1A_1'$, and $\tilde{D}^3,1A_2''$ states and vertical excitation energies were determined. The excited states were found to result from excitation of an electron from the nonbonding lobe orbital to Rydberg-like excited orbitals.

Experimentally vertical transitions have been observed at 6.39, 7.93, 8.26, and 9.25 eV; the first three have been assigned by Harshbarger [4] as excitations from the ground state to the \tilde{A}^1A_2'' , \tilde{B}^1E'' , and \tilde{C}^1A_1'

states, respectively, while the fourth may be assigned as an excitation to the \tilde{D}^1A_2'' state [11]. The corresponding triplet states have not been experimentally observed, however, Compton et al. [3], using a threshold SF_6 electron scavenger technique, have reported a low-lying transition at 4.4 eV which they suggest is due to a triplet state.

Our best calculated results for vertical excitation energies (eV) [12] are 6.140 ($^3A_2''$), 6.370 ($^1A_2''$), 7.860 ($^3E''$), 7.877 ($^1E''$), 7.865 ($^3A_1'$), 8.145 ($^1A_1'$), 8.844 ($^3A_2''$), and 8.855 ($^1A_2''$). In addition, we find no evidence for the existence of the low-lying triplet state reported by Compton et al. [3].

2. Computational details and results

The experimental ground state geometry was used [13]:

$$R_{N-H} = 1.0079 \text{ \AA} \quad \text{and} \quad \angle HNH = 107.30^\circ.$$

The double zeta basis of Huzinaga [14] and Dunning [15] was used [(9s, 5p/4s) primitive gaussians contracted to (4s, 2p/2s)], but with a set of 3d polarization functions [16] and a set of diffuse functions [17] [(3s, 2p) to better describe Rydberg orbitals] included on the nitrogen.

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2.1. GVB calculations

2.1.1. The ground state

The ground state Hartree–Fock wavefunction of ammonia consists of five doubly-occupied orbitals,

$$\psi_{\text{HF}} = \mathcal{A}\{\phi_{1a_1}^2 \phi_{2a_1}^2 \phi_{1e_x}^2 \phi_{1e_y}^2 \phi_{3a_1}^2 \alpha\beta \cdots \alpha\beta\}. \quad (1)$$

The HF wavefunctions of the low-lying excited states consist of four doubly occupied orbitals and two singly-occupied orbitals. In general, the correlation error in a closed-shell HF ground state is significantly greater than the correlation error in the open-shell excited states. This manifests itself in erroneously low HF excitation energies.

In a GVB wavefunction [18] all orbitals are singly-occupied and the spin function is completely general; For ammonia, this would lead to ten non-orthogonal orbitals. However, in our calculations, we dealt with an intermediate case in which the nitrogen 1s-like orbital is kept doubly-occupied, while each of the bond pairs and the lobe orbital were correlated. Each bond pair was correlated with two orbitals as usual in GVB calculations

$$\phi_i(1)\phi_i(2) \rightarrow \phi_{ia}(1)\phi_{ib}(2) + \phi_{ib}(1)\phi_{ia}(2) \quad (2)$$

and these orbitals were solved for in terms of the natural orbitals

$$\phi_{ia}\phi_{ib} + \phi_{ib}\phi_{ia} \rightarrow C_1^2 \bar{\phi}_{ai} \bar{\phi}_{ai} + C_2^2 \bar{\phi}_{bi} \bar{\phi}_{bi}. \quad (3)$$

For the lone pair of the ground state we included all dominant correlations (in-out and angular) leading to a pair function of the form

$$C_1^2 \phi_1^2 + C_2^2 \phi_2^2 + C_3^2 \phi_3^2 + C_4^2 \phi_4^2. \quad (4)$$

The resulting wavefunction is then the product of a doubly-occupied N 1s-like orbital times three bond functions of the form (2) times a lone pair function of the form (4). This wavefunction is multiplied by an appropriate spin function and antisymmetrized, and the orbitals are then optimized self-consistently with the restriction that the orbitals in different pairs be orthogonal and that the spin function be the simple valence bond spin function. These restrictions were removed by subsequent configuration interaction (CI) calculations. This wavefunction is sometimes denoted as GVB(4) to indicate that four pairs of electrons are correlated.

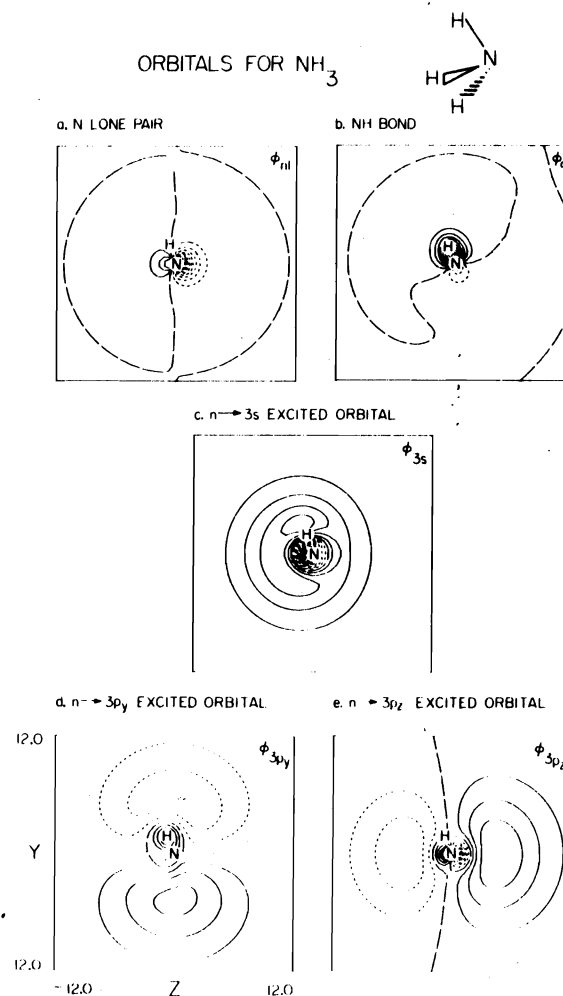


Fig. 1. NH_3 orbitals. (a, b) GVB first natural orbitals for one of the bond pairs and for the lone pair of the ground state; (c) GVB excited orbital for the A^1A_2' ($n \rightarrow 3s$) excited state; (d, e) IVO excited orbitals for the B^1E' ($n \rightarrow 3p_y$) and C^1A_2' ($n \rightarrow 3p_z$) excited states. Long dashes indicate nodal lines. Other lines are separated by equal increments of 0.05 au for (a, b) and 0.01 au for (c, d, e). The plot scale is in bohr = 0.529177 Å.

The first natural orbital from (4), ϕ_{n1} , and the first natural orbital from (3), $\phi_{\sigma1}$, for one of the bond pairs are shown in fig. 1a.

2.1.2. Excited states

Self-consistent GVB calculations were carried out

Table 1
Vertical excitation energies for ammonia (eV)

	HF	GVB(1) a)	GVB(4) b)	CI	Experimental c)
Ground state	0	0	0	0	0
3s triplet	5.251	5.798	5.930	6.140	
3s singlet	5.481	6.029	6.129	6.370	6.392
3p _x triplet	6.798	7.346	7.747 d)	7.860	
3p _x singlet	6.851	7.398	7.747 d)	7.877	7.927
3p _z triplet			7.643 d)	7.865	
3p _z singlet			7.821 d)	8.145	8.258
4s triplet			8.694 d)	8.844	
4s singlet			8.701 d)	8.855	9.25
Ion	9.405				10.85 e)

a) The NH bond pairs were not correlated.

b) The wavefunction described in section 2.1.

c) Electron impact results of W.R. Harshbarger [4].

d) Obtained from IVO calculations described in section 2.1.2.

e) D.W. Turner, C. Baker, A.D. Baker, and C.R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley-Interscience, New York, 1970) p. 357.

Table 2
Calculated total energies in hartree atomic units (1 h = 27.2116 eV)

	HF	GVB(1)	GVB(4)	CI
Ground state	-56.19918	-56.21932	-56.26842	-56.30105
³ A ₂ '' (n → 3s) a)	-56.00623		-56.05052	-56.07541
¹ A ₂ '' (n → 3s)	-55.99775		-56.04317	-56.06695

on the lowest excited triplet and singlet states. Each state has the character of a transition from the non-bonding orbital ϕ_n to a 3s-like Rydberg orbital, ϕ_{3s} , and hence is denoted as

$n \rightarrow 3s$.

In these GVB calculations the three bond pairs are described as in (3), however, the lone pair (4) is replaced by

$$(\phi_n \phi_{3s} \pm \phi_{3s} \phi_n) \quad (5)$$

for the singlet and triplet states, respectively. The 3s-like orbital of the singlet state is shown in fig. 1c.

In D_{3h} symmetry (the expected geometry for such excited states) these states give rise to ³A₂'' and ¹A₂'' symmetry. The calculated vertical excitation energies (see tables 1 and 2) are 5.930 eV for $\tilde{a}^3 A_2''$ (n → 3s) and 6.129 eV for $\tilde{A}^1 A_2''$ (n → 3s). The experimental vertical excitation energy for the singlet state is 6.392 eV indicating $\sim \frac{1}{4}$ eV of differential correlation

effects in the GVB description.

Due to the diffuseness of the excited orbitals, we expect that the core orbitals (1s orbital, bonding orbitals, and the singly-occupied lobe) would differ little between Rydberg excited states of the same spin multiplicity. Consequently the method of improved virtual orbitals [19] (IVO) was used to obtain excited orbitals for the higher excited states, in preparation for configuration interaction calculations. The IVO technique uses core orbitals from a prior self-consistent calculation (in this case core orbitals were obtained by GVB solution of the 3s singlet and triplet excited states) and solves self-consistently for the singly-occupied excited orbitals of a given spin multiplicity (without varying the core orbitals). The 3p_x, 3p_y and 3p_z excited orbitals from such calculations should be well described. We also retained the 4s-like orbital, although the basis is less adequate for it. Diffuse d functions were not included and hence we cannot describe the 3d excited states expected to lie in the vicinity of

the 4s excited state. Excitation energies from the IVO calculations are listed in table 1 for comparison with subsequent results [20]. IVO singlet–triplet splittings for the A_1 states are expected to be somewhat lower than exact values because orthogonality of the excited 1A_1 states to the ground state is not treated rigorously (the effect is small here, ~ 0.03 eV).

2.2. CI calculations

The basis orbitals for the CI calculations of the ground state consisted of all the GVB natural orbitals (eleven orbitals) except the nitrogen 1s orbital (which was kept doubly-occupied). All configurations resulting from single excitations from the basic configuration (first configuration of table 3) were included, where σ_i and σ_i^* refer to the bonding and antibonding NOs of bond pair i and the n_i refers to the NOs for the lone pair. To generate additional configurations, the set of natural orbitals was separated into four sets: $(\sigma_1\sigma_1^*)$, $(\sigma_2\sigma_2^*)$, $(\sigma_3\sigma_3^*)$, and (n_1, n_2, n_3, n_4) and intra-group excitations to a total order of four over this entire space were included. The principal configurations [21] are included in table 3.

For the excited states the CI calculation was based on the GVB orbitals of the $^1A_2''$ ($n \rightarrow 3s$) state to which we added the four (singlet) IVO orbitals (corresponding to $3p_x$, $3p_y$, $3p_z$, and 4s character) and the dominant correlating orbital (n_2) from the ground state (orthogonalized to the previous orbitals). The CI wavefunction for $^3A_2''$ ($n \rightarrow 3s$) was based on the corresponding GVB orbitals of the $^3A_2''$ ($n \rightarrow 3s$) state and the four (triplet) IVO orbitals. However, for the $n \rightarrow 3p_{x,y}$ and $n \rightarrow 4s$ states slightly lower energies

(0.02 eV) were obtained from the CI using the singlet orbitals as described above.

For the excited state the configurations for the CI calculations were selected as follows:

(i) we included all single excitations from the dominant configuration of each of the five excited states (for the singlet case the ground state configuration was also included);

(ii) partitioning the orbitals into four subsets

(σ_1, σ_1^*) , (σ_2, σ_2^*) , (σ_3, σ_3^*) ,

$(n_1, n_2, 3s, 3p_x, 3p_y, 3p_z, 4s)$,

we allowed all *intra*-group excitations from each dominant configuration with the restriction that not more than two groups are simultaneously excited (thus no excitations of order greater than four).

Principal configurations for the 3s and $3p_z$ Rydberg like excited states are given in table 4. Principal configurations for the other excited states are identical to those of the $3p_z$ Rydberg except for occupancy of the appropriate excited state orbital.

In order to eliminate the possibility of the existence of a low-lying valence triplet state (below 6 eV) which might not have been converged to in the prior computations, an additional GVB calculation was performed. In this calculation a wavefunction modeling a triplet $\sigma \rightarrow \sigma^*$ transition in one of the bond pairs was calculated. The vertical excitation energy was found to be several volts above the experimental ionization potential.

Only limited calculations were performed on the ammonia ion. In addition to the Hartree–Fock result (see table 1) a small CI calculation for the ion using

Table 3
Principal configurations of the CI wavefunction for the ground state of NH_3

Character ^{a)}	Number of cases	Orbital											Energy lowering per case (mh) ^{b)}
		σ_1	σ_1^*	σ_2	σ_2^*	σ_3	σ_3^*	n_1	n_2	n_3	n_3		
HF	1	2	0	2	0	2	0	2	0	0	0	0	—
GVB(σ)	3	2	0	0	2	2	0	2	0	0	0	0	15.6
GVB(n)	1	2	0	2	0	2	0	0	2	0	0	0	15.5
IP(σ, n)	3	2	0	1	1	2	0	1	1	0	0	0	9.5
IP(σ_i, σ_j)	3	1	1	2	0	1	1	2	0	0	0	0	3.5

^{a)} IP indicates an interpair correlation.

^{b)} 1 mh = 10^{-3} h = 0.0272116 eV = 0.62751 kcal/mole.

Table 4
Principal configurations for excited states of NH₃

Character	Number of cases	Orbital													Energy lowering per case (mh)
		σ_1	σ_1^*	σ_2	σ_2^*	σ_3	σ_3^*	n_1	n_2	3s	3p _x	3p _y	3p _z	4s	
\tilde{A}^1A_2'' HF	1	2	0	2	0	2	0	1	0	1	0	0	0	0	
GVB(σ)	3	2	0	2	0	0	2	1	0	1	0	0	0	0	13.5
IP(σ_i, σ_j)	3	2	0	1	1	1	1	1	0	1	0	0	0	0	3.1
IP(σ, n)	3	1	1	2	0	2	0	0	1	1	0	0	0	0	2.6
\tilde{C}^1A_1' HF	1	2	0	2	0	2	0	1	0	0	0	0	1	0	
GVB(σ)	3	2	0	0	2	2	0	1	0	0	0	0	1	0	13.3
IP(σ_i, σ_j)	3	2	0	1	1	1	1	1	0	0	0	0	1	0	3.0
IP(σ, n)	3	1	1	2	0	2	0	0	1	0	0	0	1	0	2.5

GVB(4) ground-state orbitals as a basis was performed. The configurations involved corresponded to ionization of an electron from the lobe orbital or from one of the three bonding orbitals. The purpose of this calculation was to determine the contribution of the configuration corresponding to ionization from the lobe orbital relative to that of configuration corresponding to ionization from the bonding orbitals. The results of this calculation indicate that the lowest ionization occurs predominantly (89%) from the lobe orbital.

3. Comparison with other calculations

Horsley and Flouquet [7] carried out Hartree–Fock calculations on the ground state and the lowest lying singlet and triplet excited states. They used a minimal basis set and obtained adiabatic excitation energies of 3.56 eV for the singlet and 3.95 eV for the triplet. (Note: In this calculation the triplet excitation energy was greater than that of the corresponding singlet.) These values are about 2 eV too low.

Much cruder Hartree–Fock calculations were carried out by Bishop et al. [8] who used a single-center expansion and obtained approximate Hartree–Fock calculations for the excited states. The ground state energy and excitation energies were *not* reported.

Higuchi [5] carried out minimal basis Hartree–Fock calculations using approximate integrals and obtained a vertical excitation energy of 6.7 eV for the $^1A_1 \rightarrow ^1A_2''$ transition. The agreement with the experimental value is remarkable considering the approxima-

tions made and limitations of the basis set (which did not include a nitrogen 3s orbital).

The semi-empirical CNDO technique has been applied to the $\tilde{X}^1A_1 \rightarrow \tilde{A}^1A_2''$ adiabatic transition by Kroto and Santry [6]. Their calculated excitation energy was 6.80 eV compared with the 5.72 eV experimental value [10].

4. Summary

We find that relatively simple GVB calculations including CI among the GVB orbitals leads to excellent excitation energies (average error ~ 0.06 eV). We find that the lower excited states are of Rydberg character with very small triplet–singlet splittings. No evidence was found for a low lying (below 6 eV) triplet state (using the ground state geometry).

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