Theoret. chim. Acta (Berl.) 1, 410—417 (1963)

Department of Chemistry, Carnegie Institute of Technology, Pittsburgh 13,
Pennsylvania, USA

A One-centre Treatment of the Ammonium and Borohydride Ions

By

DAVID M. BISHOP

One-centre, five term, electronic wave functions are determined for the ammonium and borohydride ions. Total molecular energies are determined for various internuclear distances and the equilibrium internuclear distances and the breathing force constants found. These values are in agreement with the observed quantities. The proton affinity of ammonia is predicted to be 0.362 a. u.

Für die Ionen NH_4^+ und BH_4^- wird je eine fünfgliedrige Einzentren-Elektronenfunktion berechnet. Die Gesamtenergie der Moleküle wird für verschiedene Kernabstände bestimmt; daraus erhält man Gleichgewichtsabstände und Kraftkonstanten der totalsymmetrischen Schwingung. Die Werte stimmen mit dem Experiment gut überein. Die Protonenaffinität des NH_3 wird zu 0,362 at. E. berechnet.

Des fonctions électroniques monocentriques à cinq termes sont déterminées pour les ions NH_4^+ et BH_4^-. Les énergies totales des molécules sont calculées pour plusieurs distances internucléaires d'où sont tirés les distances d'équilibre et les constantes de force de la vibration symétrique. Les valeurs sont en accord avec les quantités observées. La protonaffinité du NH_3 est prédite à 0,362 unités atomiques.

Introduction

Although one-centre methods have been used to investigate the methane molecule fairly thoroughly [*4*, *24*], less attention has been given to its isoelectronic neighbours: the borohydride ion (BH_4^-) and the ammonium ion (NH_4^+). Both of these ions are tetrahedral, contain ten electrons and should be reasonably well described by a five term wave function similar to that used for the methane molecule [*4*].

Of the treatments of the ammonium ion which have been given previously, the first was by HORVATH [*17*], who distributed the protons on a sphere and used a N^{3-} wave function inside this sphere and a Na^+ wave function outside The molecular energy was calculated as -12.57 a. u. with respect to N^{5-} (this ion has an energy of -44.80 a. u. [*25*]) and consequently the total energy of the ammonium ion will be -57.37 a. u. BERNAL [*2*] using a one-centre treatment, described the electrons with an analytic one term spherical wave function; this work was later extended into a Hartree-Fock calculation as a preliminary investigation of the properties of metallic ammonium [*3*], unfortunately no energy was calculated for this extended wave function. In 1958 HARTMANN and GLIEMANN [*14*, *15*] published an analytical treatment using a spherical wave function and included a calculation of the infrared frequencies, however, their treatment was limited to the outer eight electrons. KRAUSS [*18*] has recently used the Hartree-Fock method with exponential quadratic functions and GREIN [*12*], using a single spherical determinantal wave function containing three parameters, has calculated the total molecular energy for both NH_4^+ and BH_4^-. The results of these authors are summarized in Tab. 1.

Table 1. *Predicted total molecular energies (E_0) in a. u., equilibrium bond distances (R_0) in a. u. and symmetric breathing vibrational frequencies (ν_1) in cm^{-1}*

	E_0	R_0	ν_1
NH_4^+			
HORVATH [*17*]	-57.37	1.60	—
BERNAL [*2*]	-55.68	1.84	—
HARTMANN [*15*]	—	2.00	3600*
KRAUSS [*18*]	-56.50	—	—
GREIN [*12*]	-55.68	1.84	—
BH_4^-			
GREIN [*12*]	-26.11	2.21	2189*

---

* for an eight electron wave function

Method

The present calculation follows closely that given previously [*4, 24*]. A five term wave function of the form:

$$\Psi = c_1 \Phi_1 + c_2 \Phi_2 + c_3 \Phi_3 + c_4 \Phi_4 + c_5 \Phi_5$$

is used, where the Φ are combinations of Slater determinants, which in turn are made up of spin functions α and β (indicated, respectively, by no bar and a bar) and normalized atomic orbitals centred on the heavy atom nucleus.

$$\Phi_1 = (s\, \bar{s}\, s^*\, \bar{s}^*\, p_x\, \bar{p}_x\, p_y\, \bar{p}_y\, p_z\, \bar{p}_z),$$

$$\Phi_2 = 2^{-1/2} \left[(s\, s\, s^*\, \bar{f}_{xyz}\, p_x\, \bar{p}_x\, p_y\, \bar{p}_y\, p_z\, p_z) + (s\, s\, f_{xyz}\, \bar{s}^*\, p_x\, \bar{p}_x\, p_y\, \bar{p}_y\, p_z\, \bar{p}_z)\right],$$

$$\Phi_3 = 6^{-1/2} \left[(s\, \bar{s}\, s^*\, \bar{s}^*\, p_x\, \bar{d}_{yz}\, p_y\, \bar{p}_y\, p_z\, \bar{p}_z) + (s\, \bar{s}\, s^*\, \bar{s}^*\, d_{yz}\, \bar{p}_x\, p_y\, p_y\, p_z\, \bar{p}_z) + \right.$$

$$\left. + (s\, \bar{s}\, s^*\, \bar{s}^*\, p_x\, \bar{p}_x\, p_y\, \bar{d}_{xz}\, p_z\, \bar{p}_z) + \text{etc.}\ \right],$$

$$\Phi_4 = 6^{-1/2} \left[(s\, \bar{s}\, s^*\, \bar{s}^*\, p_x\, \bar{f}_{x(5x^2-3)}\, p_y\, \bar{p}_y\, p_z\, \bar{p}_z) + \text{etc.}\ \right],$$

$$\Phi_5 = 6^{-1/2} \left[(s\, \bar{s}\, s^*\, \bar{s}^*\, p_x\, \bar{g}_{yz(7x^2-1)}\, p_y\, \bar{p}_y\, p_z\, \bar{p}_z) + \text{etc.}\ \right],$$

$$s = N_s\, r^{n_s-1} \exp(-\zeta_s\, r),$$

$$s' = N_{s'}\, r^{n_{s'}-1} \exp(-\zeta_{s'}\, r),$$

$$s^* = (s' - Ss)/(1 - S^2)^{1/2},$$

$$p_x = N_p\, r^{n_p-1} \exp(-\zeta_p\, r)\, [\sqrt{3}\, x],$$

$$d_{yz} = N_d\, r^{n_d-1} \exp(-\zeta_d\, r)\, [\sqrt{15}\, yz],$$

$$f_{xyz} = N_f\, r^{n_f-1} \exp(-\zeta_f\, r)\, [\sqrt{105}\, xyz],$$

$$f_{x(5x^2-3)} = N_{f'}\, r^{n_{f'}-1} \exp(-\zeta_f\, r)\, [\sqrt{7}\, x\, (5x^2-3)/2],$$

$$g_{yz\,(7x^2-1)} = N_g\, r^{n_g-1} \exp(-\zeta_g\, r)\, [\sqrt{45}\, yz\, (7x^2-1)/2],$$

$$N_\alpha = (2\, \zeta_\alpha)^{n_\alpha + 1/2}\, [4\pi(2n_\alpha)!]^{-1/2},$$

$$S = \int s\, s'\, d\tau.$$

x, y and z are the Cartesian co-ordinates, divided by r, the radial distance.

The coefficients, c_i, are determined by the variational method and the parameters n and n/ζ by minimization of the expectation value of the energy for given N-H or B-H bond distances. Non-integral n values are allowed and the energy formulas are derived in the standard way. All the calculations were made on the Bendix G-20 computer at the Carnegie Institute of Technology Computation Center and the minimization procedure was based on the "pattern search" method of HOOKE and JEEVES [*16*].

Unless otherwise indicated all quantities are in atomic units: length in units of $a_0 = 0.52917 \times 10^{-8}$ cm, and energies in units af $e^2/a_0 = 27.210$ eV.

Results

In Tab. 2 and 3 the best n and n/ζ values are given for a series of N-H and B-H bond distances (R); in Tab. 4 and 5 there are tabulated the total electronic energies (E^{el}), the classical nuclear interaction energies (E^{nuc}), the total molecular energies (E^{tot}), the kinetic energies (T) and the ratios of the latter two quantities for the same distances. In Tab. 6 and 7 the coefficients, c_i, are given and in Tab. 8—11 the coefficients and matrix elements for $R = 1.90$ a. u. in the ammonium ion case and $R = 2.20$ a. u. in the borohydride ion case.

From the five total molecular energies and the five total kinetic energies, predictions can be made for the equilibrium internuclear distances (R_0), the equilibrium total molecular energy (E_0) and the force constant of the symmetric breathing vibration (k). This may be done by fitting a polynomial of the form

$$a + bR + cR^2 + dR^3 + eR^4 \tag{1}$$

or

$$a + bR + cR^2 \tag{2}$$

(the latter by the method of least squares) to the total molecular energies and finding the second derivative with respect to R, this giving k and the minimum

Table 2. *Parameter values for the five-term ammonium ion wave function for different N-H distances (R)*

All quantities are in atomic units: length in units of $a_0 = 0{,}52917 \times 10^{-8}$ cm, energies in units of $e^2/a_0 = 27.210$ eV

R	1.75	1.85	1.90	1.95	2.00
n_s	0.9876	0.9877	0.9878	0.9879	0.9879
$(n/\zeta)_s$	0.1501	0.1501	0.1501	0.1501	0.1501
$n_{s'}$	2.1702	2.1149	2.0896	2.0646	2.0413
$(n/\zeta)_{s'}$	1.1087	1.1184	1.1225	1.1261	1.1291
n_p	1.6366	1.6079	1.5942	1.5809	1.5680
$(n/\zeta)_p$	1.1770	1.2039	1.2169	1.2296	1.2420
n_d	5.5942	5.6758	5.7150	5.7548	5.7931
$(n/\zeta)_d$	1.7741	1.8640	1.9090	1.9542	1.9995
n_f	8.4191	8.4860	8.5150	8.5419	8.5641
$(n/\zeta)_f$	1.7584	1.8431	1.8852	1.9271	1.9687
$n_{f'}$	8.7970	8.9090	8.9641	9.0149	9.0652
$(n/\zeta)_{f'}$	1.8348	1.9317	1.9801	2.0287	2.0772
n_g	9.7582	9.8563	9.9040	9.9520	9.9971
$(n/\zeta)_g$	1.8481	1.9446	1.9928	2.0410	2.0892

Table 3. *Parameter values for the five-term borohydride ion wave function for different B-H distances (R)*

R	2.0	2.1	2.2	2.3	2.4
n_s	0.9823	0.9824	0.9825	0.9826	0.9827
$(n/\zeta)_s$	0.2139	0.2139	0.2139	0.2138	0.2138
$n_{s'}$	2.4211	2.3690	2.3159	2.2634	2.2104
$(n/\zeta)_{s'}$	1.6731	1.7054	1.7358	1.7643	1.7907
n_p	1.8193	1.7991	1.7781	1.7566	1.7345
$(n/\zeta)_p$	1.8428	1.8995	1.9554	2.0107	2.0652
n_d	5.7237	5.8220	5.9180	6.0123	6.1054
$(n/\zeta)_d$	2.1320	2.2254	2.3191	2.4131	2.5073
n_f	8.4497	8.5534	8.6506	8.7429	8.8312
$(n/\zeta)_f$	2.1081	2.1992	2.2902	2.3812	2.4721
$n_{f'}$	8.7432	8.8668	8.9865	9.1042	9.2189
$(n/\zeta)_{f'}$	2.1591	2.2581	2.3572	2.4562	2.5553
n_g	9.6853	9.8053	9.9217	10.0337	10.1425
$(n/\zeta)_g$	2.1858	2.2858	2.3857	2.4856	2.5854

Table 4. *Electronic energy (E^{el}), classical nuclear interaction energy (E^{nuc}), total molecular energy (E^{tot}), kinetic energy (T) and the ratio of the latter two quantities for different N-H distances (R)*

R	1.75	1.85	1.90	1.95	2.00
E^{el}	−74.348318	−73.390449	−72.940802	−72.509186	−72.094584
E^{nuc}	18.099563	17.121208	16.670650	16.243197	15.837117
E^{tot}	−56.248755	−56.269241	−56.270152	−56.265988	−56.257467
T	56.957034	56.493970	56.285372	56.091461	55.912205
T/E^{tot}	−1.012592	−1.003994	−1.000270	−0.996898	−0.993863

Table 5. *Electronic energy (E^{el}), classical nuclear interaction energy (E^{nuc}), total molecular energy (E^{tot}), kinetic energy (T) and the ratio of the latter two quantities for different B-H distances (R)*

R	2.00	2.10	2.20	2.30	2.40
E^{el}	−38.341595	−37.797460	−37.290638	−36.817480	−36.374797
E^{nuc}	11.837117	11.273445	10.761016	10.293145	9.864264
E^{tot}	−26.504478	−26.524015	−26.529622	−26.524335	−26.510533
T	27.157541	26.861322	26.596943	26.379430	26.166917
T/E^{tot}	−1.024640	−1.012717	−1.002538	−0.994537	−0.987039

Table 6. *The linear coefficients (c_k) for different N-H distances (R) in the ammonium ion*

R	1.75	1.85	1.90	1.95	2.00
c_1	0.913313	0.910633	0.909361	0.908123	0.906913
c_2	0.130522	0.129481	0.128771	0.127945	0.126992
c_3	0.338412	0.342851	0.344961	0.347012	0.349035
c_4	−0.117480	−0.120972	−0.122656	−0.124319	−0.125950
c_5	0.143177	0.147648	0.149795	0.151889	0.153925

Table 7. *The linear coefficients (c_k) for different B-H distances (R) in the borohydride ion*

R	2.0	2.1	2.2	2.3	2.4
c_1	0.875451	0.870611	0.866003	0.861605	0.857394
c_2	0.172304	0.174435	0.176187	0.177607	0.178718
c_3	0.394802	0.400498	0.405763	0.410657	0.415220
c_4	−0.139998	−0.144340	−0.148487	−0.152445	−0.156246
c_5	0.168609	0.174287	0.179737	0.184973	0.190040

Table 8. *Wave functions for the ammonium ion at $R = 1.90$ a. u. Ψ_k is a k-term wave function of the form $\Sigma c_i \Phi_i$ with the linear coefficients given in this table and the non-linear parameter values given in Tab. 2. centre column. The value of E^{tot} at the bottom of each column is the total molecular energy at $R = 1.90$ a. u. for the wave function indicated at the top of the column*

	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5
c_1	1.000000	0.990238	0.929680	0.918951	0.909361
c_2		0.139384	0.132273	0.129459	0.128771
c_3			0.343802	0.352376	0.344961
c_4				− 0.120836	− 0.122656
c_5					0.149795
E^{tot}	−55.967464	−56.016755	−56.162435	−56.195035	−56.270152

Table 9. *Wave functions for the borohydride ion at $R = 2.20$ a. u. Ψ_k is a k-term wave function of the form $\Sigma c_i \Phi_i$ with the linear coefficients given in this table and the non-linear parameter values given in Tab. 3, centre column. The value of E^{tot} at the bottom of each column is the total molecular energy at $R = 2.20$ a. u. for the wave function indicated at the top of the column*

	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5
c_1	1.000000	0.977270	0.889362	0.874850	0.866003
c_2		0.211999	0.186781	0.180346	0.176187
c_3			0.417310	0.424378	0.405763
c_4				− 0.148379	− 0.148487
c_5					0.179737
E^{tot}	−26.182237	−26.255360	−26.415341	−26.451283	−26.529622

Table 10. *Matrix elements between the component functions of the five-term ammonium ion wave function, at $R = 1.90$ a. u. (nuclear-nuclear repulsions included)*

	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5
Φ_1	−55.967464	− 0.350178	− 0.392499	0.210911	− 0.459916
Φ_2		−53.528965	− 0.066269	—	− 0.078026
Φ_3			−55.075576	0.208583	− 0.140465
Φ_4				−53.982808	0.112217
Φ_5					−52.995712

Table 11. *Matrix elements between the component functions of the five-term borohydride ion wave function, at $R = 2.20$ a. u. (nuclear-nuclear repulsions included)*

	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5
Φ_1	−26.182237	− 0.337084	− 0.345914	0.187257	− 0.407722
Φ_2		−24.701475	− 0.048712	—	− 0.057944
Φ_3			−25.656333	0.174900	− 0.112572
Φ_4				−24.846978	0.093011
Φ_5					−24.177375

of each curve giving R_0 and E_0. Alternatively one may fit the values of T/E^{tot} to polynomials of the form

$$-1 + aR + bR^2 + cR^3 + dR^4 + eR^5 \tag{3}$$

or

$$-1 + aR + bR^2 + cR^3 \tag{4}$$

(the latter, once again, by the method of least squares) and evaluate k from: $k = -E_0 \, [d(T/E^{\text{tot}})/dR]_0/R_0$ and R_0 as the point where $T/E^{\text{tot}} = -1$. These quantities are tabulated in Tab. 12 and 13 as well as the vibrational frequencies which are derived from the expression $k = 16\,\pi^2\, m_H\, \nu_1^2\, c^2$.

Experimental Values

In Tab. 12 and 13 a number of experimental values appear that require some comment. The equilibrium internuclear distances have been found from the line breadths in the N.M.R. spectra of the ammonium halides [*13, 26*] and $NaBH_4$ [*11*].

Table 12. *Predicted internuclear N-H distances (R_0) in a. u., breathing force constants (k) in md/Å, frequencies (ν_1) in cm^{-1} and equilibrium energies (E_0) in a. u. using the four equations (1—4) (see text) respectively and the energy values for the five N-H distances: 1.75, 1.85, 1.90, 1.95, 2.0 a. u.*

	R_0	k	ν_1	E_0
equation 1	1.883	33.2	3736	— 56.2704
equation 2	1.890	34.2	3797	— 56.2704
equation 3	1.904	32.4	3691	—
equation 4	1.904	32.8	3719	—
observed	1.956	—	> 3252	— 56.8415

Table 13. *Predicted internuclear B-H distances (R_0) in a. u., breathing force constants (k) in md/Å, frequencies (ν_1) in cm^{-1} and equilibrium energies (E_0) in a. u. using the four equations (1—4) (see text) respectively and the energy values for the five B-H distances: 2.0, 2.1, 2.2, 2.3, 2.4 a. u.*

	R_0	k	ν_1	E_0
equation 1	2.197	17.0	2674	— 26.5296
equation 2	2.211	17.2	2695	— 26.5297
equation 3	2.228	15.5	2556	—
equation 4	2.228	16.8	2660	—
observed	2.370	—	2265	— 27.205

Until 1960 the fundamental vibrational frequency (ν_1) of the ammonium ion was taken to be 3041 ± 2 cm^{-1}, this value coming from investigations of the Raman spectra of NH_4Cl [*7, 21*], however, recently MATHIEU and POULET [*20*] from their work on the Raman spectra of NH_4PF_6 have suggested that for the free ion ν_1 is at least as great as 3252 cm^{-1}. The value of $\nu_1 = 2265$ cm^{-1} for the borohydride ion is taken from the work of EMERY et al. on the Raman spectra of $LiBH_4$ in liquid ammonia [*9, 10, 27*].

The experimental value of the total molecular energy of the ammonium ion (— 56.8415 a. u.) can be calculated from the total energy of ammonia, — 56.5645 a. u. [*8*], and the proton affinity of ammonia, on which LAMPE and FIELD [*19*] put the lower limit of 174 kcal/mole (0.277 a. u.).

The heat of formation of the borohydride ion has been found to be -23 ± 5 kcal/mole at 298.16°K [1], this value together with the heat of formation of hydrogen atoms and the heat of sublimation of boron [23] gives $\Delta H_0^{298.16} = -328.56$ kcal/mole for the reaction:

$$B(g) + 4H + e^- = BH_4^-.$$

If it is assumed that the difference in the heat of this reaction at 0° K and 298.16° K is the same as the difference for the reaction

$$C\,(g) + 4\,H = CH_4$$

[6, 23] then $\Delta H_0^0 = -323.47$ kcal/mole or -0.515 a. u. The energy of boron is -24.657 a. u. [22] and therefore the total molecular energy of the borohydride ion is -27.172 a. u. To this must be added the zero point vibrational energy, which is calculated from EMERY et al. [9] to be 0.033 a. u. giving a final total molecular energy of -27.205 a. u.

Discussion

The results presented in this paper are all comparable in accuracy to those computed for the methane molecule [4]. The total molecular energy of the ammonium ion is better than all previous calculations save one [18] and of the borohydride ion better than the one other previous calculation [12]. It is not surprising that the wave function of KRAUSS [18] should give a lower molecular energy for the ammonium ion; it contains nineteen basis orbitals compared with seven in the present work, and thirty one linear coefficients compared with five in the present work. Equilibrium bond distances are also close to the experimental values. The non-degenerate fundamental frequencies are within 17% of the experimental values and it is apparent that for this quantity the spherical wave function [12] is better than the non-spherical wave function given here; this fortuitous phenomenon was also found for methane [4].

In a recent paper BISHOP et al. [5] have calculated, using a spherical wave function, the total molecular energy of ammonia to be -55.605 a. u.: in Tab. 8 the energy of NH_4^+ for the spherical term alone is given as -55.967. Consequently one can make the prediction that the proton affinity of ammonia is $+0.362$ a. u., a value in agreement with the experimental lower limit of 0.277 a. u. [19].

Finally it is interesting to note that the parameters n and n/ζ follow changes in bond distance almost exactly in a linear fashion.

It is a pleasure to acknowledge many useful discussions with Professor R. G. PARR. This work was supported by a research grant to Carnegie Institute of Technology from the American Chemical Society — Petroleum Research Fund.

Literature

[1] ALTSHULLER, A. P.: J. Amer. chem. Soc. **77**, 5455 (1955).
[2] BERNAL, M. J. M.: Proc. physic. Soc. **A 66**, 514 (1953).
[3] —, and H. S. W. MASSEY: M. Notices Roy. Astr. Soc. London **114**, 172 (1954).
[4] BISHOP, D. M.: Mol. Physics **6**, 305 (1963).
[5] —, J. R. HOYLAND and R. G. PARR: Mol. Physics **6**, 467 (1963).
[6] BREWER, L., and A. W. SEARCY: Ann. Rev. physic. Chem. **7**, 259 (1956).
[7] COUTURE, L., and J. P. MATHIEU: J. Chim. physique **49**, 226 (1952).
[8] DUNCAN, A. B. F.: J. chem. Physics **27**, 423 (1957).

[9] Emery, A. R., and R. C. Taylor: J. chem. Physics **28**, 1029 (1958).
[10] — — and D. R. Schultz: J. Amer. chem. Soc. **80**, 27 (1958).
[11] Ford, P. T., and R. E. Richards: Disc. Farad. Soc. **19**, 230 (1955).
[12] Grein, F.: Theoret. chim. Acta (Berl.) **1**, 52 (1962).
[13] Gutowsky, H. S., G. E. Pake and R. Bersohn: J. chem. Physics **22**, 643 (1954).
[14] Hartmann, H.: Zeitschr. Naturforsch. **2a**, 489 (1947).
[15] —, u. G. Gliemann: Z. physik. Chem. [Frankfurt a. M.] **15**, 108 (1958).
[16] Hooke, R., and T. A. Jeeves: J. Assoc. comput. Mach. 8, 212 (1961).
[17] Horvath, J. I.: J. chem. Physics **16**, 851, 857 (1948).
[18] Krauss, M.: J. chem. Physics **38**, 564 (1963).
[19] Lampe, F. W., and F. Field: Tetrahedron **7**, 189 (1959).
[20] Mathieu, J. P., and H. Poulet: Spectrochimica Acta **16**, 696 (1960).
[21] Menzies, A. C., and H. R. Mills: Proc. Roy. Soc. London **A 148**, 407 (1935).
[22] Moore, C. E.: Atomic Energy Levels, N.B.S. Circular 467, Washington 1949.
[23] Rossini, F. D.: Selected Values of Chemical Thermodynamic Properties, N.B.S. Circular 500, Washington 1952.
[24] Saturno, A. F., and R. G. Parr: J. chem. Physics **33**, 22 (1960).
[25] Scherr, C. W., J. H. Silverman and F. A. Matsen: Physic. Rev. **127**, 830 (1962).
[26] Stevenson, D. P., and J. A. Ibers: Ann. Rev. physic. Chem. **9**, 359 (1958).
[27] Woodward, L. A., and H. L. Roberts: J. chem. Soc. **1956**, 1170.

(Received July 29, 1963)