S. C. F. Study of the OH_3^+ Ion *

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A convergent self consistent field calculation for the OH_3^+ ion is reported. The results indicate that the isolated ion is planar, with an OH distance of 1.9007 a.u. (=1.006 Å nearly), self consistent field energy of −76.3722 a.u., and force constants of $k_1 = 6.84 \times 10^5$ dynes/cm and $k_\Delta / l^2 = 2.39 \times 10^5$ dynes/cm.

The correlation contribution to the binding energy for several ten electron systems are analysed in the Appendix.

The existence and structure of OH_3^+ in crystalline hydrates of strong acids has been shown by nuclear magnetic resonance, infra-red, Raman and X-ray spectra, and in liquid water by infra-red spectra. From these results it appears that the ion has a flat pyramidal structure with a bond distance of about 1.9842 a.u. (1.02 Å) and a HOH angle of $115^\circ - 117^\circ$. The force constant for the OH bond is estimated to be $(6.29 \pm 0.05) \times 10^5$ dynes/cm. (See reference [1].) Reported values [2] of the proton affinity of H_2O vary between 169 kcal/mole and 200 kcal/mole. Recently, Lampe and Futrell [3] have recalculated Sherman's [4] estimate (based on crystal energies and Born–Haber thermochemical cycles) and conclude that the revised value is 8.14 eV or 0.299 a.u. If one accepts this value for the proton affinity of H_2O, the molecular energy of OH_3^+ is −76.764 a.u. (since the experimental energy of H_2O is −76.465 a.u.).

Recently Grahn [1] in a theoretical study of the isolated ion has obtained energies of the ion using an OH distance of 1.8108 a.u. (0.9581 Å) and HOH angle equal to 100°, 110° and 120°. This value of the OH distance was used by the author because it enabled him to use the molecular integrals calculated by Ellison and Shull [5] and Ellison [6] for the H_2O molecule, using Slater type of atomic orbitals as basic functions. Subsequently Gaspar et al. [2] have reported an S.C.F. one-centre calculation with OH distance of 1.71 a.u., HOH angle of 120° and using Slater functions. Later Moscowitz and Harrison [7] have reported an S.C.F. calculation for different OH distances and HOH angles and using Gaussian functions.

In this paper an S.C.F. calculation of the isolated OH_3^+ ion is reported. Three planar configurations with OH distances of 1.7 a.u., 1.9 a.u. and 2.1 a.u. and one tetrahedral configuration with an OH distance of 1.9 a.u. and HOH angle of 115° have been studied. Basis functions of the Slater type have been used.

The method of calculation is briefly described in Section I, and the results are reported and discussed in Section II.

I. The Method of Wave Function Calculations

For closed shell systems the Hartree–Fock wave function is a single determinant of doubly occupied orbitals, φ_p i. e.

$$\Phi = \mathcal{A}(\varphi_1 \alpha \, \varphi_1 \beta \, \varphi_2 \alpha \, \varphi_2 \beta \dots \varphi_N \alpha \, \varphi_N \beta) \qquad (1)$$

where $\mathcal{A}$ is the anti-symmetrizing operator and α, β are the spin functions. Koopmans [8] showed that this is achieved by taking for φ the eigenfunctions of the one electron Hamiltonian

$$F \equiv K + V + 2 \sum_{j=1}^{N} \mathrm{d}\boldsymbol{r}_2 \, \varphi_j^*(\boldsymbol{r}_2) \, \varphi_j(\boldsymbol{r}_2) \, r_{12}^{-1} - \sum_{j=1}^{N} \mathrm{d}\boldsymbol{r}_2 \, \varphi_j^*(\boldsymbol{r}_1) \, \varphi_j(\boldsymbol{r}_2) \, r_{12}^{-1} \, P(\boldsymbol{r}_2/\boldsymbol{r}_1) \qquad (2)$$

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* Read at the Zurich Symposium (March—April 1966) on Theoretical Chemistry.

[1] For an extensive bibliography see R. Grahn, Arch. Phys. **19**, 147 [1961].

[2] See, for instance, R. Gaspar, I. Tamassy-Lentei, and Y. Kruglyak, J. Chem. Phys. **36**, 740 [1962], Table IV.

[3] F. W. Lampe and J. H. Futrell, Trans. Faraday Soc. **59**, 1957 [1963].

[4] J. Sherman, Chem. Rev. **11**, 93 [1932].

[5] F. O. Ellison and H. Shull, J. Chem. Phys. **23**, 2348 [1955].

[6] F. Ellison, J. Chem. Phys. **23**, 2358 [1955].

[7] J. W. Moscowitz and M. C. Harrison, J. Chem. Phys. **43**, 3550 [1965].

[8] T. C. Koopmans, Physica **1**, 104 [1933].

where $P(\mathbf{r}_2/\mathbf{r}_1)$ is defined to replace $\mathbf{r}_1$ by $\mathbf{r}_2$. KOOPMANS has also shown that in this form a good approximation to the ionized system was obtained by leaving out one of the orbitals.

The variational approximation to the eigenfunctions of this operator are given by assuming that

$$\varphi_i = \sum_{j=1}^{n} X_j^i \zeta_j \tag{3}$$

and solving the eigenvalue problem

$$\sum_{j=1}^{n} \{ (\zeta_t | F | \zeta_s) - E^i (\zeta_t | G | \zeta_s) \} X_s^i = 0 \tag{4}$$

where n is greater than N, and $(\zeta_t | G | \zeta_s)$ is the overlap matrix. Since F is dependent on the X_s^i it is only feasible to solve this by an iteration method in which the last approximation to the φ_i is used in the evaluation of F.

In the present calculation, the technique of accumulative accuracy [9, 10] has been used and the calculated energies are expected to be very close to the HARTREE–FOCK energies. The phrase accumulative accuracy implies that at any stage it is possible to restart with a wave function that has been calculated before and improve it further, without being concerned about the details of that calculation. This characteristic can be incorporated into any calculation provided that the integrals of the form $(\varphi\varphi : \varphi\varphi)$ where $\varphi = \Sigma X \zeta$ are calculated directly, instead of through the constituent integrals $(\zeta\zeta : \zeta\zeta)$.

A method of numerical integration has been used in the present calculation. The use of numerical methods has two advantages. In making the assumption (3) the first N ζ's are linear combinations of functions of the form $P(x, y, z, r) \times \exp(-\zeta r)$ (in other words the first N ζ's are φ's obtained in an earlier iteration) and these ζ's are "improved" by means of the remaining $(n-N)$ functions which are single functions. The second advantage is that earlier iterations have been performed with coarse grids of points, thus economising on machine time. The computer programs for carrying out the calculations are described in reference [10].

II. Results of the Calculation

The three hydrogen atoms are taken to form an equilateral triangle. In the planar configuration the oxygen atom is at the centre of gravity of the triangle. Three planar configurations with OH distances of 1.7 a. u., 1.9 a. u. and 2.1 a. u have been studied. In the tetrahedral case the oxygen atom is on a perpendicular to the plane of the hydrogen atoms passing through the centre of gravity. One tetrahedral configuration with an OH distance of 1.9 a. u. and HOH angle of 115° has been considered. This corresponds to a height of 0.4315 a. u. above the plane of the hydrogen atoms.

In each case seventeen basis functions of the form $P(x, y, z, r) \times \exp(-\zeta r)$ have been used. These are $\exp(-7.75\,r)$, $(r, x, y, z, r x, r y, r z, x y, y z, z x, x^2, y^2, z^2) \times \exp(-2.275\,r)$ centred on the oxygen atom and $\exp(-1.2\,r)$ centred on each hydrogen atom.

The calculated eigenvalues and molecular energies for the different configurations are given in Table 1. The energies of the planar configurations were expressed as a quadratic expression of the OH distance. This gave an energy minimum of -76.3722 a. u. and the minimum distance for OH was 1.9007 a. u. (=1.006 Å nearly). The force constant for the OH bond calculated from this quadratic expression is 6.8353×10^5 dynes/cm und may be compared with the value of 6.31×10^5 dynes/cm given by TAYLOR and VIDALE [11] for the tetrahedral OH_3^+ in perchlorate ion with an HOH angle of about 117°.

		Planar		Tetrahedral OH=1.9 a. u.; HOH=115°
	OH=1.7 a. u.	OH=1.9 a. u.	OH=2.1 a. u.	
ε_1	−21.2118	−21.2017	−21.1969	−21.2076
ε_2	− 1.8031	− 1.8004	− 1.7981	− 1.8232
ε_3	− 1.2288	− 1.2115	− 1.1975	− 1.2058
ε_4	− 1.2288	− 1.2115	− 1.1975	− 1.2058
ε_5	− 1.0339	− 1.0004	− 0.9691	− 1.0037
Mol energy	−76.34406	−76.37214	−76.34753	−76.35761

Table 1. Calculated eigenvalues and energies of the OH_3^+ ion (all entries in atomic units).

For the configurations with an OH distance of 1.9 a. u., the planar configuration is energetically 0.01453 a. u. lower than the tetrahedral one and hence the planar configuration is concluded to be the more stable one.

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[9] S. F. BOYS and P. RAJAGOPAL, Advan. Quantum Chemistry, Vol. II, Edited by P. O. LOWDIN, Academic Press, New York 1965, p. 1.

[10] P. RAJAGOPAL, Z. Naturforschg. **20 a**, 1557 [1965].

[11] R. C. TAYLOR and G. L. VIDALE, J. Am. Chem. Soc. **78**, 5999 [1956].

The energy difference of the planar and tetrahedral configurations has been expressed as a quadratic in distance of the oxygen atom above the H_3 plane. This gives a force constant of

$$k_\Delta/l^2 = 2.38870 \times 10^5 \text{ dynes/cm.}$$

No comparable experimental figures are available.

All ab initio calculations of wave functions of polyatomic molecules known as the LCAO-MO method [12] make the assumption (3) and solve the eigenvalue problem (4). However, the specific form of the ζ's and the points in space where they are centred are at the choice of each worker. The results of three other calculations and those of the present calculations are given in Table 2. Only planar configuration results are quoted in the Table. For the present work, the results given by a calculation with eight basis functions are also included, to facilitate comparison.

Appendix

Correlation Contribution to the binding energy

The phrase "correlation energy" appears to have been first used by WIGNER and SEITZ [13] in their investigations on metallic sodium. When the wave function is assumed to be a determinant of single electron functions, "this leads to correlations between electrons of parallel spin and to none whatever between electrons of anti-parallel spin. There are such correlations, however, arising from the mutual repulsion terms, but they lie beyond the scope of FOCK's equations. We shall call these holes "correlation holes" and the corresponding energy "correlation energy"."

If the true solution of the SCHROEDINGER equation is Ψ and the HARTREE–FOCK solution Ψ_{HF}, GREEN et al. [14] have suggested writing

$$\Psi = C_1 \, \Psi_{\mathrm{HF}} + \Psi_{\mathrm{corr}}$$

with the orthogonality requirement

$$\int \Psi^*_{\mathrm{corr}} \, \Psi_{\mathrm{HF}} \, d\tau = 0 \, .$$

Then correlation energy is defined as

$$E_{\mathrm{exact}} - | C_1 |^2 E_{\mathrm{HF}} \, .$$

They go on to remark that "however C_1 is not usually known and hence it has been usual to assume that correlation energy is the difference between the experimental and HARTREE–FOCK energies, recognising that this method yields only the lower limit".

A concise summary of the present situation with references to the literature are given by GIMARC and PARR [15]. The carrying out of GREEN's prescription requires both the exact eigenfunction of the HAMILTONIAN used and the convergent HARTREE–FOCK wave function.

It is essential to obtain the HARTREE–FOCK wave functions and energies before a consideration of correlation effects is possible. Also the HARTREE–FOCK wave functions and energies are sufficiently important by themselves, because electronic properties most often measured are those whose corresponding operators are one electron operators and the HARTREE–FOCK wave functions are expected to give good results for these [16].

	GRAHN [1]	GASPAR et al. [2]	MOSCOWITZ and HARRISON [7]		This work	
			(1)	(2)	(1)	(2)
Basis set	SLATER functions	SLATER functions One centre method	GAUSSian functions of the form $f(x, y, z) \times \exp(-\zeta r^2)$		SLATER type of functions	
Number of basis functions used	8	5*	23	42	8	17
OH distance	1.8106 a.u.	1.71 a.u.	1.8 a.u.	1.8 a.u.	1.9 a.u.	1.9 a.u.
Ionisation Potentials:	0.9392 a.u. 1.1356 a.u.		0.9480 a.u. 1.1620 a.u.	0.9411 a.u. 1.1591 a.u.	0.9691 a.u. 1.1681 a.u.	1.0004 a.u. 1.2115 a.u.
Molecular energy	− 76.1820 a.u.	− 75.4120 a.u.	− 75.8460 a.u.	− 76.3213 a.u.	− 76.1914 a.u.	− 76.3722 a.u.

* The non-linear parameters are varied to obtain minimum energy.

Table 2. Results of selected calculations for OH_3^+ (planar configurations only).

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[12] For some remarks on this acronym and its inadequacy see R. S. MULLIKEN, J. Chem. Phys. **43**, S 39 [1965].

[13] E. WIGNER and F. SEITZ, Phys. Rev. **46**, 509 [1934]. — See also E. WIGNER, ibid. **46**, 1002 [1934].

[14] L. C. GREEN, M. M. MULDER and P. C. MILNER, Phys. Rev. **91**, 35 [1953].

[15] B. M. GIMARC and R. G. PARR, Ann Rev. Phys. Chem. **16**, 451 [1965].

[16] See CHR. MØLLER and M. S. PLESSET, Phys Rev. **46**, 618 [1934].

[17] See, for instance, P. O. LOWDIN, Advan. Chem. Phys. **2**, 207 [1959]. — S. F. BOYS and G. B. COOK, Rev. Mod. Phys. **32**, 285 [1960].

	NH_3	CH_4	HF	H_2O	OH^-	NH_4^+	OH_3^+	BH_4^-
Binding energy	0.480[21]	0.677[23]	0.223[25]	0.370[28]	0.190[29]	(0.813)	(0.698)	0.584[31]
Experimental energy of atoms	N 54.602 3H 1.5	C 37.846 4H 2.0	F 99.810 H 0.5	O 75.095 2H 1.0	O^- 75.162 H 0.5			B 24.657 3H 1.5
Proton affinity of						NH_3 0.338[3]	H_2O 0.299[3]	H^- 0.528
Experimental energy of						NH_3 56.582	H_2O 76.465	
Experimental energy of molecule	56.582	40.523	100.533	76.465	75.852	56.920	76.764	27.269
Hartree-Fock energy of molecule	56.236[22]	40.181[24]	100.058[26] 100.089[27]	76.042[7] (76.089)	75.367[7] (75.434)	56.534[22]	76.372[30]	(26.933)
Hartree-Fock energy of separated atoms[19]	55.901	39.689	99.909	75.809	75.289	55.901	75.809	26.529
Hartree-Fock binding energy	0.335	0.492	0.149 0.180	0.233 (0.280)	0.078 (0.145)	0.633	0.563	(0.404)
Correlation contribution to binding energy	0.145	0.185	0.074 0.043	0.137 (0.090)	0.112 (0.045)	(0.180)	(0.135)	(0.180)
Lower limit to molecular correlation energy including relativistic energy	0.346	0.342	0.475 0.444	0.423 (0.376)	0.485 (0.418)	0.386	0.392	(0.336)
Lower limit to molecular correlation energy including relativistic energy minus correlation contribution to binding energy	0.201	0.157	0.401	0.286	0.373	0.206	0.257	(0.156)
Experimental energy of atoms minus Hartree-Fock energy of atoms[20]	N^4S 0.201	C^3P 0.157	F^2P 0.401	O^3P 0.286	$O^{-2}P$ 0.373			B^2P 0.128 H^- 0.028

Table 3. Analysis of results for several ten electron systems. (All quantities in the table are negative but the minus sign has been suppressed. All quantities are in atomic units. Quantities in brackets are estimates; see text.)

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[19] All figures in this row, except that for O^- are quoted from E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 [1962]. — The value for O^- is from C. C. J Roothaan and P. S Kelly, Phys. Rev. **131**, 1177 [1963].

[20] All figures in this row are obtained by subtracting SCF energy of atoms [19] from experimental energy.

[21] Obtained by adding dissociation energy given by S. R. Gunn and L. C. Green, J. Phys. Chem. **65**, 779 [1961] to the zero point energy of −0.033 a. u.

[22] Unpublished work of this author; see also Z. Naturforschg. **20 a**, 1557 [1965].

[23] Obtained by adding dissociation energy given by Gunn and Green [21] to the zero point energy of −0.044 a. u.

[24] B. J. Woznick, J. Chem. Phys. **40**, 2860 [1964].

[25] J. W. C. Johns and R. F. Barrow, Proc. Roy. Soc. A **251**, 504 [1959].

[26] E. Clementi, J. Chem. Phys. **36**, 33 [1962].

[27] R. Moccia, J. Chem. Phys. **40**, 2176 [1964].

[28] Obtained by adding dissociation energy given by Gaspar et al. [2] to the zero point energy of −0.021 a. u.

[29] Obtained by adding the dissociation energy as estimated by Gaspar et al. [2] and a zero point energy of −0.010 a. u.

[30] This work; see Table 1.

[31] A. P. Altshuller, J. Am. Chem. Soc. **77**, 5455 [1955].

The difficulties of obtaining the exact eigenfunction of the HAMILTONian for polyatomic systems is well known[17]. However since there are few interesting properties of atoms or molecules that depend on two electron operators other than the energy itself, other approaches to estimating this quantity have been investigated.

In this appendix we collect the available results on several ten electron systems and investigate the possibility of estimating some unknown quantities. The correlation contribution to the binding energy (hereafter referred to as CCTBE) is defined as the difference between the binding energy of the molecule and the HARTREE–FOCK contribution to the binding energy (see Fig. 1). A similar analysis has been made for CH_4 and NH_4^+ by KRAUSS[18]. Subsequently several results on these and other systems have been reported, which are brought together in Table 3.

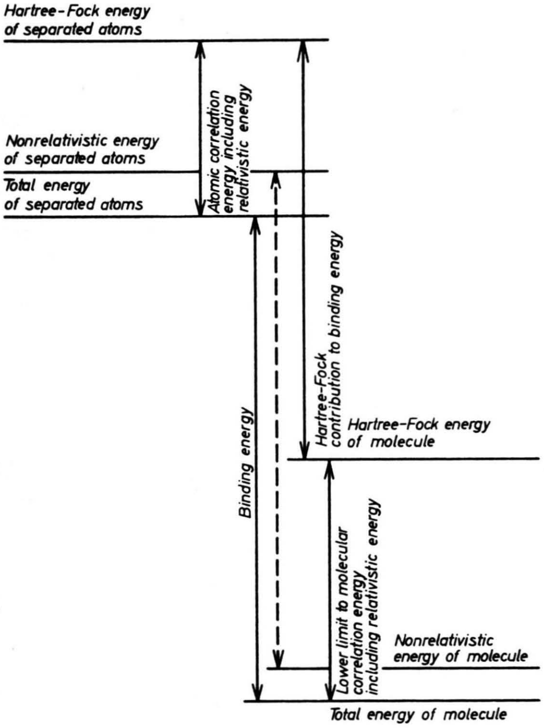

Fig. 1. Correlation contribution to binding enery = Binding energy minus HARTREE–FOCK binding energy. (Not drawn to scale.)

The value of CCTBE for NH_3 and CH_4 are -0.145 a. u. and -0.185 a. u. respectively. In the case of the HF molecule there exists an estimate of the SCF energy which leads to a CCTBE of -0.043 a. u. The experimental energy of NH_4^+ in Table 3 has been obtained by adding the energy of NH_3 to its proton affinity. An alternative way of arriving at this quantity would be to add the binding energy of NH_4^+ (-0.769 a. u. given by KRAUSS), its zero point energy which has been taken to be -0.040 a. u. (zero point energies of NH_3 and CH_4 are -0.033 a. u. and -0.044 a. u. respectively) and the experimental energies of the separated atoms, which gives -56.911 a. u. which is quite close to the value of -56.920 a. u. in the table. The value used in the table for the binding energy gives a CCTBE of -0.176 a. u.

From these CCTBE values of -0.145 a. u., -0.185 a. u., -0.043 a. u., and -0.176 a. u. for NH_3, CH_4, HF and NH_4^+ respectively, it appears that CCTBE is about -0.045 a. u. per bond. Using this value we may estimate the SCF energies of OH_2, OH^- and BH_4^- to be -76.089 a. u., -75.434 a. u., and -26.933 a. u. respectively and the binding energies of OH_3^+ and NH_4^+ to be 0.698 a. u. and 0.813 a. u. respectively.

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Notes added in proof

1. Using a minimal basis set of HARTREE–FOCK atomic orbitals, KAPLAN[32] has reported an energy of -56.266 a. u. for the NH_3 molecule. JOSHI[33] has given cogent arguments (see also CADE's remarks in the discussion following JOSHI's paper) as to why KAPLAN's result is probably erroneous.

2. After the present work was communicated the author saw the work of KRAUSS[34] where the S.C.F. energy of BH_4^- is reported to be -27.946 a. u.

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[18] M. KRAUSS, J. Chem. Phys. **38**, 564 [1963].

[32] H. KAPLAN, J. Chem. Phys. **26**, 1074 [1957].

[33] B. D. JOSHI, J. Chem. Phys. **43**, S 40 [1965].

[34] M. KRAUSS, J. Res. Nat. Bur. Stand. **68 A**, 635 [1964].