Convergent S. C. F. Wave Function and Properties of the Ammonia Molecule

P. RAJAGOPAL

Max-Planck-Institut für Physik und Astrophysik, München

(Z. Naturforschg. **20 a**, 1557—1565 [1965]; received 23 August 1965)

A self consistent field wave function calculation for the ammonia molecule by the technique of accumulative accuracy is described. The molecular integrals required are calculated by numerical integration methods. Total and dissociation energies, dipole and quadrupole moments and ionization potentials calculated using the wave function are reported. The proton affinity of NH_3 is also estimated.

It is well known that if electronic stationary state wave functions can be evaluated for the various configurations of a system of atomic nuclei, then most of the spectral, chemical and physical properties of the corresponding system of atoms can be calculated. This is true when the atoms form a stable molecule or when the system corresponds to an unstable configuration of atoms such as occur in the intermediate stages of a chemical reaction. Hence this general problem includes, in principle, a large number of problems in theoretical chemistry and a converging method of solution would effectively solve these problems.

At present the main method which provides practical procedures for the accurate calculation of many electron wave functions and energies is that of configurational interaction. In this method the wave function is expressed in the form

$$\Psi = \sum_i Y_i \, \Phi_i \qquad (1)$$

where the wave function Ψ is expanded as a linear combination of SLATER determinants constructed from orthonormal single electron functions, the coefficients being determined by the RITZ variational method[1]. The self consistent field method[2] is the approximation of using a single determinant Φ and then adjusting some or all of the implicit parameters in this function to obtain a stationary value of the energy. This method cannot converge to the true solution of the SCHRÖDINGER equation, but for the prediction of many physical properties it is a sufficient approximation. It may also be regarded as the first term in the expression for Ψ above and so its calculation can be regarded as an intermediate step in the general calculation.

Most of the molecular wave function calculations that have been performed till now have been done in the self consistent field framework (with limited configurational interaction) but have not reached the HARTREE–FOCK limit. For a complete bibliography we refer to ALLEN and KARO's paper[3] and to SLATER's book on molecular structure[4]. Recently, a method of successive approximation by which the stationary state electronic wave function for any configuration of atoms can be calculated to any desired degree of accuracy in the self consistent field limit, using the technique of accumulative accuracy was described[5]. This implies that at any stage, it is possible to restart from the best result previously determined, or from the best result of some other workers or even with an approximation guessed from any external evidence. This aspect has not appeared to such an extent in previous methods of wave function calculations for polyatomic systems. It was, in fact, a characteristic of the one dimensional integration method for atoms by the HARTREE–FOCK technique.

The characteristic of accumulative accuracy can be incorporated into any calculation, provided integrals of the form $(\varphi\varphi : \varphi\varphi)$ where $\varphi = \sum_i X_i \, \eta_i$ are calculated directly, instead of through the constituent integrals $(\eta\eta : \eta\eta)$. A method of numerical integra-

---

[1] See for instance, S. F. BOYS and G. B. COOK, Rev. Mod. Phys. **32**, 285 [1960].

[2] D. R. HARTREE, Proc. Cambridge Phil. Soc. **24**, 89, 111, 246 [1928]. — V. FOCK, Z. Phys. **61**, 126 [1930]. — J. C. SLATER, Phys. Rev. **35**, 210 [1930].

[3] L. C. ALLEN and A. M. KARO, Rev. Mod. Phys. **32**, 275 [1960].

[4] J. C. SLATER, Quantum Theory of Molecules and Solids, Vol. I, McGraw-Hill, New York 1963.

[5] S. F. BOYS and P. RAJAGOPAL, Advances in Quantum Chemistry, Vol. II, edited by P. O. LÖWDIN, Academic Press, New York, to be published in 1965.

tion is used in the sequel. This has the advantage that integrals can be evaluated for a much wider range of expansion functions, η, than previously and the necessary integrals can be obtained directly instead of by laborious transformations of simpler integrals.

The accumulative accuracy characteristic and the integral calculation methods are considered in sections I and II. A wave function calculation for the NH_3 molecule is described in section III and the properties of the molecule obtained by using this wave function are given in section IV. A discussion of the method and the results follow in section V.

We shall be concerned with the many electron SCHRÖDINGER equation for stationary states. We shall express it in atomic units * and denote it as

$$H\,\Psi \equiv \{\sum_i K_i - \sum_{I,i} Z_I V_{Ii} + \tfrac{1}{2}\sum_{i,j} M_{ij}\}\,\Psi = E\,\Psi \qquad (2)$$

where

$$K_i \equiv -\frac{1}{2}\left\{\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right\},$$

$$V_{Ii} = \{(x_i - A_{Ix})^2 + (y_i - A_{Iy})^2 + (z_i - A_{Iz})^2\}^{-1/2},$$

$$M_{ij} = \{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2\}^{-1/2},$$

where x_i, y_i, z_i, v_i are the space and spin variables corresponding to the total number of electrons, where A_{Ix}, A_{Iy}, A_{Iz} are the positions of the nuclei which are to be regarded as fixed and with integral charges Z. Ψ is a function antisymmetric with respect to the different sets of variables (x_i, y_i, z_i, v_i).

The notation $(\,|\;|\,)$ will be used to denote integration over all the space coordinates and summation over all the spin variables of the contained functions, the complex conjugate of the first function being taken. The same notation will be used for many- and single-electron functions, and for functions dependent on space and spin variables or only on either space or spin variables. The integrals are independent of the variables of integration and these will generally by omitted, thus

$$(f_r\,|\,V_I\,|\,f_s) = \int \mathrm{d}\mathbf{r}\, f_r^*(\mathbf{r})\, f_s(\mathbf{r})\, r_I^{-1}. \qquad (3)$$

It is also convenient to define

$$\begin{aligned}(f_r f_t\,|\,M\,|\,f_s f_u) &= \iint \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, f_r^*(\mathbf{r}_1)\, f_s(\mathbf{r}_1)\, f_t^*(\mathbf{r}_2)\, f_u(\mathbf{r}_2)\, r_{12}^{-1} \\ &= (f_r f_s : f_t f_u). \qquad (4)\end{aligned}$$

The single electron integrals which arise, then, are $(f_r\,|\,G\,|\,f_s)$, $(f_r\,|\,K\,|\,f_s)$, and $(f_r\,|\,V_I\,|\,f_s)$ where the first of these types of integrals are the overlap integrals, the symbol G having been introduced into the bracket for future reference and the double electron integrals are of the type $(f_r f_s : f_t f_u)$.

It will be assumed that when the integrals required are calculable, the system of functions

$$r_k^p\, x_k^q\, y_k^s\, z_k^t \exp(-a_k r_k) \qquad (5)$$

is the most direct one to use and will be referred to as η functions. The suffix k has been used to number the occupied electronic shells of the atoms, with r_k the distance from the corresponding nucleus and a_k the SLATER exponent for the particular shell [6]. We shall refer to the functions as s, p, d, ... functions when the polynomial multiplying the exponential part is of degree 0, 1, 2, ... respectively. Such a system of functions is many times overcomplete but its early terms will give a satisfactory approximation to the wave function. The use of overcomplete systems of functions does not create any difficulties in principle and in practice the detailed problems raised by the overcompleteness are easily solved.

Energy values which are accurate to 1 kcal/mole are referred to as chemical accuracy.

I. The Technique of Accumulative Accuracy

For a $2N$ electron system with electrons in N doubly occupied orbitals, the aim of the S.C.F. calculation is to find the best single determinant function

$$\Phi = \mathcal{A}(\varphi_1\alpha\, \varphi_1\beta\, \varphi_2\alpha\, \varphi_2\beta \ldots \varphi_N\alpha\, \varphi_N\beta) \qquad (7)$$

which gives the lowest energy. α and β are the spin functions. KOOPMANS [7] showed that this is achieved by taking for φ the eigenfunctions of the single electron HAMILTONian

$$\begin{aligned}F \equiv K + V &+ \sum_{j=1}^{N} \mathrm{d}\mathbf{r}_2\, \varphi_j^*(\mathbf{r}_2)\, \varphi_j(\mathbf{r}_2)\, r_{12}^{-1} \\ &- \sum_{j=1}^{N} \mathrm{d}\mathbf{r}_2\, \varphi_j^*(\mathbf{r}_1)\, \varphi_j(\mathbf{r}_2)\, r_{12}^{-1}\, P(\mathbf{r}_2\,|\,\mathbf{r}_1)\end{aligned} \qquad (8)$$

where $P(\mathbf{r}_2\,|\,\mathbf{r}_1)$ is defined to replace $\mathbf{r}_1$ by $\mathbf{r}_2$. F is dependent on the orbitals themselves and so

---

* Atomic units are derived by setting $\hbar = e = m = c = 1$. 1 a. u. of length = 0.52917 Å, 1 a. u. of energy = 27.20 ev = 627.41 kcal/mole.

[6] J. C. SLATER, Phys. Rev. **36**, 57 [1930].

[7] T. C. KOOPMANS, Physica **1**, 104 [1933].

could only be solved by an iteration procedure. However, it is the same F depending on the orbitals symmetrically for all the orbitals. 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

$$\varphi_i = \sum_{j=1}^{n} X_j^i \, \bar{\eta}_j \tag{9}$$

and solving the eigenvalue problem

$$\sum_{s}^{n} \{ (\bar{\eta}_t \,|\, F \,|\, \bar{\eta}_s) - E^i \, (\bar{\eta}_t \,|\, G \,|\, \bar{\eta}_s) \} \, X_s^i = 0 \,, \tag{10}$$

where n is greater than N. Since, if F is written out fully, it is dependent on the X_s^i, it is only feasible to solve this by an iterative method in which the last approximation to the φ_i is used in the evaluation of F.

Let φ_i^- be the best estimates to the φ_i from data available before the current iteration and let F^- be the operator in terms of these. Then in the accumulative procedure the φ_i^- are used both for F^- and for the first N of the $\bar{\eta}_k$ set. The remaining $(n-N)$ of the $\bar{\eta}_k$ set are functions which are estimated as likely to be most effective in improving the φ_i^-. When the F and G matrices have been computed and the eigenvalue problem has been solved, the N lowest eigenfunctions are the best approximations to the orbitals and we refer to them as φ_i^+. The φ_i^+ are therefore linear combinations of the $\bar{\eta}_k$ set obtained by improving the φ_i^- with the $(n-N)$ improvement functions. This is only one step of the iteration and the φ_i^+ are not yet the best S.C.F. orbitals which may be obtained from the $\bar{\eta}_k$ set. The process is now repeated using the φ_i^+ as the first N of the $\bar{\eta}_k$ set and $n-N$ improvement functions.

In the whole procedure, there are two iteration processes. One is caused by the S.C.F. convergence using a limited basis set and the other is due to the need for the repeated use of different subsets of improvement functions. If we use the same set $\bar{\eta}_k$, but the improvement functions are chosen in rotation and repeated until convergence is achieved, we obtain the S.C.F. wave function with the limited basis set. But if we introduce new improvement functions before S.C.F. convergence has been achieved within a limited basis set, the adjustment of F appears to proceed in the background while the other relaxations are being effected.

In the earlier analytical procedures, eqs. (9) and (10) are still the same except that $\bar{\eta}_k$ are SLATER type of functions and eqs. (10) are the familiar ROOTHAAN's equations [8]. If integrals of the form $(\varphi\varphi : \varphi\varphi)$, where $\varphi = \sum_i X_i \, \eta_i$ are expanded in terms of $(\eta\eta : \eta\eta)$, this requires the computation of more than $n^4/8$ of these. Hence the integral computation increases as $C\,n^4$. In fact there are other aspects concerned with the manipulation and transformation of the $(\eta \,|\, F \,|\, \eta)$ matrices which increase the factor to the fifth power although these are not so extensive until n exceeds 20 or so. If on the other hand the $(\varphi\varphi : \varphi\varphi)$ integrals are calculated by evaluating $\varphi^2(\boldsymbol{r}_1)\, \varphi^2(\boldsymbol{r}_2)\, r_{12}^{-1}$ at a number of integration points, the only increase is in the evaluation of $\varphi = \sum_i X_i \, \eta_i$ at each point, and hence the computation increases merely as n. The constant of proportionality is rather large when sufficient points for chemical accuracy are used, so that for small n the amount of computation is much greater in the new method than in the older ones. But for large n the saving in effort is considerable.

II. Description of the Integral Calculations

The most difficult integrals which have to be evaluated are of the type

$$(\varphi\varphi : \varphi\varphi) = \iint \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \, \varphi^2(\boldsymbol{r}_1) \, \varphi^2(\boldsymbol{r}_2) \, r_{12}^{-1} \tag{11}$$

where the φ behave like $\exp(-a\, r_I)$ in the neighbourhood of the various nuclei. The φ^2 or $\varphi_i \, \varphi_j$ in the general case, are somewhat different in form from the φ_i but they show these same characteristics. The conditions are extremely unfavourable for numerical integration. The following is a device by which any function $F(r)$ of the $\varphi_i^2(\boldsymbol{r})$ type can be expanded into components each having only one cusp. For detailed reasons, it is better to make a further subdivision so that the components correspond to the electronic shells of the atoms.

The component functions, F_s, are defined by

$$F_s(\boldsymbol{r}) = F(\boldsymbol{r}) \, V_s(\boldsymbol{r}) / \sum_t V_t(\boldsymbol{r}) \,. \tag{12}$$

It will be seen that

$$F(\boldsymbol{r}) = \sum_s F(\boldsymbol{r}) \, V_s(\boldsymbol{r}) \, / \sum_t V_t(\boldsymbol{r}) = \sum_s F_s(\boldsymbol{r}) \,. \tag{13}$$

The $V_s(r)$ are to be chosen so that V_s is larger than all other V_t in the region where the orbitals of the

---

[8] C. C. J. ROOTHAAN, Rev. Mod. Phys. **23**, 69 [1951].

s-th electronic shell are greater than those of other shells. It is easiest to see the significance of this when there is just one shell per atom. In this case a satisfactory set of V_s functions is given by $1/r_I^4$ where r_I are the distances from the various nuclei. It is apparent that as r approaches the I-th nucleus, $1/r_I^4$ tends to infinity with F_I tending to F and all other F_J tending to zero. Hence none of the F_J $(J \neq I)$ has a cusp at I.

When there are two shells, as in the N atom, these extend to such different distances from the nucleus that it is desirable to split the component function for these regions into different parts and to integrate these with different sets of points. For the NH_3 molecule, it can be seen that the functions V in the following set cause such a resolution. The letters N and H refer to the nitrogen and hydrogen atoms.

$$V_1 = j/r_N{}^4; \quad V_2 = (1-j)/r_N{}^4;$$
$$V_3 = 1/r_{H1}{}^4; \quad V_4 = 1/r_{H2}{}^4; \quad V_5 = 1/r_{H3}{}^4 \quad (14)$$

where

$$j = [1 + \exp\{2(r_N/D - 1)\}]^{-1}.$$

The value 0.45 assigned to D was approximately three times the radius of the inner shell.

Each $F(\boldsymbol{r})$ is resolved into the sum of five functions, so that the evaluation of a general electrostatic integral can now be performed by the evaluation of twentyfive integrals of the type $(F_s(\boldsymbol{r}_1):F_t(\boldsymbol{r}_2))$, the latter being integrals between single centre functions.

When an integral of the form $(C(\boldsymbol{r}_1) : D(\boldsymbol{r}_2))$ is calculated by the simplest method of taking a discrete set of points $(s = 1, 2, \ldots)$ associated with the weights U_s in three-dimensional space, a result of the following form is obtained:

$$\iint \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \, C(\boldsymbol{r}_1) \, D(\boldsymbol{r}_2) \, r_{12}{}^{-1} = \sum_s \sum_t C(\boldsymbol{r}_s) \, D(\boldsymbol{r}_t) \, U_s U_t \, |\boldsymbol{r}_s - \boldsymbol{r}_t|^{-1}. \quad (15)$$

It is apparent that this is unreliable because if the same points are used for both the three dimensional spaces then infinite terms occur for $\boldsymbol{r}_s = \boldsymbol{r}_t$.

This difficulty is avoided by using the formula

$$\iint \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \, C(\boldsymbol{r}_1) \, D(\boldsymbol{r}_2) \, r_{12}{}^{-1} \quad (16)$$
$$= \sum_s \sum_t C(\boldsymbol{r}_s) \, D(\boldsymbol{r}_t) \, U_s U_t \, (r_{st}{}^3 + \lambda \, U_s^{1/2} \, U_t^{1/2})^{-1/3}.$$

Electrostatic arguments were used to find λ so that when $\boldsymbol{r}_s$ and $\boldsymbol{r}_t$ approach each other the appropriate value for the interaction of two charge distributions is obtained (see reference [5]). λ was found to be $2^{-3/2}$ but was replaced by 3^{-1}, because the final result is very insensitive to the value of this coefficient.

The way in which a numerical integration procedure is valid for high or low order functions is easily seen by considering the three dimensional integrals such as $(\varphi_1 | G | \varphi_2)$ and $(\varphi_1 | K | \varphi_2)$ where φ_1 and φ_2 are either single terms of the type in (5) or linear combinations of such terms. At each point P used in the numerical integration φ_1, φ_2 and $K\varphi_2$ are evaluated. The detailed method provides a weighting factor $U(P)$. Then the contributions to the total integrals are merely

$$U(P) \, \varphi_1(P) \, \varphi_2(P) \quad \text{and} \quad U(P) \, \varphi_1(P) \, K \varphi_2(P).$$

The value of

$$K \varphi_2(P) = -\tfrac{1}{2} \nabla^2 \varphi_2(P)$$

is obtained by evaluating the general formula for the derivative of each term $r^p x^q y^s z^t \exp(-a r)$ in terms of p, q, s, t, and a and adding these together. When the integration points have been chosen by a procedure such as described in Appendix I, no singularities arise in these integrals and the amount of computation only varies according to the computation required for each φ. This increases with the number of terms but not appreciably with the values of p, q, s, and t.

For six-dimensional integration of the type $(\varphi_i \varphi_j : \varphi_k \varphi_l)$ once the combinations of points P and Q in the $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ spaces have been chosen, it is only necessary to evaluate $\varphi_i^* \varphi_j$ at P and $\varphi_k^* \varphi_l$ at Q. In most cases all the orbitals φ that are used will be real; so it is only necessary to evaluate $\varphi_i \varphi_j$ at P and $\varphi_k \varphi_l$ at Q. Here again, the nature of the terms occuring in the φ have no significant effect on the procedure of computation. The increase in complexity in $x^3 \exp(-a r)$ compared with $\exp(-a r)$, for example, is practically negligible compared with the evaluation of r and the exponential functions. In using the programs which are in operation at present there is no feeling of an extra barrier if higher order functions of the type (5) are used.

It may be asked whether it is worthwhile producing three dimensional integrals by numerical integration, because of the magnitude of these integrals. When φ is a linear combination of SLATER type of functions, evaluating integrals between such functions and later transforming them into φ integrals results in a loss of accuracy. This is particularly so when the number of functions which constitute a φ

increases. Also, it was considered desirable that all integrals be calculated on a uniform basis. In fact the individual three dimensional integrals provided a powerful check both on integration methods and detecting programming errors.

There is also the programming effort to be considered; programs now in use have been written for the IBM 7090 computer in about half a year.

III. Wave Functions of NH_3 in the SCF Limit

a) Molecular Geometry and Basis Functions

The nitrogen atom is taken to be at the centre and the three hydrogen atoms at the three vertices of a cube (Fig. 1). The only parameter that need be specified is the edge, a of the cube. There does not appear to be great point in placing atoms at the minimum energy positions in calculations of this type and it is more systematic to take several configurations and interpolate between these for the minimum energy. The calculation reported here is done with $a = 2.2$ a.u. and this gives a distance $NH = 1.9053$ a.u. and an angle $HNH = 109° 30'$. The expansion function on the hydrogen atoms was chosen as $\exp(-1.2\, r_H)$ and those on the nitrogen atoms as $\exp(-6.7\, r_N)$ and $P(x, y, z, r) \exp(-1.95\, r_N)$ where $P(x, y, z, r)$ is a polynomial. All first and second degree polynomials (r, x, y, z; rx, ry, rz, x^2, y^2, z^2, xy, yz, zx) and six of the third degree polynomial (r^2x, r^2y, r^2z, rx^2, ry^2, rz^2) have been used. The other third degree polynomial terms were dropped after one iteration. Even those f functions which are used do not seem to be of significance for purposes of chemical accuracy.

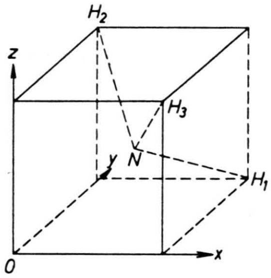

Fig. 1. The coordinate axis for the NH_3 and NH_4^+ wave function calculations.

b) The Wave Function Calculation

The calculation described here may be considered to fall into three stages. The first stage is the calculation of the wave function with s and p functions on the nitrogen atom and s function on each hydrogen atom. The next two stages are the inclusion of d functions and f functions respectively on the nitrogen atom.

The calculation was started with $\exp(-6.7\, r)$ and $r \exp(-1.95\, r)$ on N and $\exp(-1.2\, r)$ on each H and the functions $x \exp(-1.95\, r)$, $y \exp(-1.95\, r)$ and $z \exp(-1.95\, r)$ were used as improvement functions. Earlier iterations were performed with a coarse grid and the last two iterations were done with a fine grid to get an accurate value of the energy.

Given the initial orbitals and the improvement functions, the three and the six dimensional matrices are calculated and G and F matrices are set up. When the eigenvalues problem is solved, we have the new orbitals expressed as linear combinations of the initial orbitals (φ^-) and the improvement functions. Some of the η's will appear both in the initial orbitals φ^- and in the improvement functions; it is convenient to have the orbitals expressed as linear combinations of η's. Since the three and the six dimensional integrals are calculated using different grids of points (see Appendix II) the resulting orbitals are orthonormalized with the grid of points used for the six dimensional integrals by the symmetric method of Löwdin [9]. These are the orbitals referred to as φ^+ and form the starting point for the next iteration.

It must be noted that there is one feature which is a little regrettable. The total energy of an approximation found in one iteration is only evaluated in the next iteration. It could be calculated as a separate item but this would involve nearly as much computation as for the next iteration without providing the next adjustment. So it is most conveniently regarded as obtained in the next step. It is well known that the total energy for some doubly occupied orbitals φ_i is

$$W = \sum_{i=1}^{N} (\varphi_i \,|\, F(\varphi_i) \,|\, \varphi_i) + \sum_{i=1}^{N} (\varphi_i \,|\, K + V \,|\, \varphi_i) \tag{17}$$

where the F operator is dependent on the same φ_i. The quantity

$$\sum_{i=1}^{N} (\varphi_i^- \,|\, F(\varphi_i^-) \,|\, \varphi_i^-) \tag{18}$$

is the sum of the first N diagonal elements in the eigenvector matrix in the calculation of φ_i. Further,

---

[9] P. O. Löwdin, Adv. Physics 5, 1 [1956].

Basis function	Orbital 1	Orbital 2	Orbital 3	Orbital 4	Orbital 5	Molecular Energy (a.u.)
$\exp(-1.2\,r)$	-0.0049	0.1582	0.3515	-0.3544	0.1108	
$\exp(-1.2\,r)$	-0.0050	0.1583	-0.4827	-0.1272	0.1108	
$\exp(-1.2\,r)$	-0.0049	0.1579	0.1312	0.4816	0.1108	
$\exp(-6.7\,r)$	0.9956	-0.2100	0.0000	0.0000	0.0752	
$r\exp(-1.95\,r)$	0.0226	0.7364	0.0000	0.0000	-0.4077	
$x\exp(-1.95\,r)$	0.0021	0.0725	0.4650	0.1225	0.5275	
$y\exp(-1.95\,r)$	0.0021	0.0725	-0.1264	-0.4638	0.5268	
$z\exp(-1.95\,r)$	0.0022	0.0723	-0.3386	0.3414	0.5277	-56.0036
$rx\exp(-1.95\,r)$	0.0012	-0.0113	-0.0011	0.0026	-0.0289	
$ry\exp(-1.95\,r)$	-0.0027	0.0411	0.0033	-0.0025	0.0118	
$rz\exp(-1.95\,r)$	0.0017	-0.0285	0.0036	-0.0015	0.0161	
$x^2\exp(-1.95\,r)$	0.0063	-0.0161	-0.0291	0.0188	0.0075	
$y^2\exp(-1.95\,r)$	0.0011	0.0122	0.0153	-0.0202	0.0102	
$z^2\exp(-1.95\,r)$	0.0009	0.0031	-0.0231	-0.0107	-0.0037	
$xy\exp(-1.95\,r)$	-0.0016	0.0008	-0.0011	-0.0037	0.0091	
$yz\exp(-1.95\,r)$	-0.0004	0.0017	0.0018	0.0021	-0.0077	
$zx\exp(-1.95\,r)$	0.0011	-0.0014	0.0032	-0.0035	-0.0015	-56.2215
$r^2x\exp(-1.95\,r)$	0.0007	-0.0005	0.0004	-0.0004	0.0014	
$r^2y\exp(-1.95\,r)$	0.0006	-0.0002	0.0008	-0.0009	0.0009	
$r^2z\exp(-1.95\,r)$	0.0000	-0.0003	0.0007	-0.0002	0.0016	
$rx^2\exp(-1.95\,r)$	-0.0000	0.0004	-0.0012	0.0010	-0.0008	
$ry^2\exp(-1.95\,r)$	-0.0000	0.0010	-0.0009	-0.0008	-0.0010	
$rz^2\exp(-1.95\,r)$	-0.0004	0.0009	0.0008	-0.0006	-0.0007	-56.2268
Orbital Energy (a.u.)	-15.4876	-1.1935	-0.5967	-0.5968	-0.3859	

Table 1. Molecular orbitals of NH_3 in S. C. F. limit. The coefficients tabulated are those of normalized basis functions. The energies in the last column are those for variational expansions up to the function shown.

the quantities $(\varphi_i^- | K+V | \varphi_i^-)$ are obtained in the construction of the F matrix, so that

$$\sum_{i=1}^{N}(\varphi_i^- | F(\varphi_i^-) | \varphi_i^-) + \sum_{i=1}^{N}(\varphi_i^- | K+V | \varphi_i^-) \qquad (19)$$

is obtained as a by-product in the calculation.

This is the most realistic test of convergence. In the last iteration to confirm that no appreciable changes in φ_i occur no appreciable change in W occurs. It must be admitted that the delay in knowing W for a particular iteration is a nuisance in the early stages of an investigation, but this is not much of a disadvantage because the iterations are continued until no significant changes in the φ_i occur.

Table 1 shows the wave functions including up to some f functions. The energies in the last column correspond to the wave functions up to that stage.

IV. Calculated Properties of NH_3

a) Total and Dissociation Energies

The total electronic energy is given by formula (19). The total molecular energy is obtained by the addition of the nuclear repulsion energy

$$\sum_{\alpha \neq \beta} Z_\alpha Z_\beta r_{\alpha\beta}^{-1},$$

the summation being over all nuclei.. The calculated molecular energy in the self consistent field limit is -56.2268 a.u. (experimental: -56.5645 a.u.) and that of the separated atoms[10] -55.9009 a.u. (experimental: -56.1090 a.u.). The self consistent field contribution to the binding energy is therefore 0.3259 a.u. (experimental: 0.4555 a.u.) (see Table 2).

b) Ionization Potentials

The two highest orbital energies are -0.3859 a.u. and -0.5967 a.u., so that the two lowest ionization potentials are 10.50 ev and 16.24 ev. Some experimental values are also given in Table 2.

c) Dipole and Quadrupole Moments

We consider the molecule as a continuous charge distribution referred to a coordinate system fixed in the molecule, with the origin at the nitrogen molecule. The moments of the molecular charge distribution are defined by the integrals,

$$\int \varrho(\boldsymbol{r})\,d\tau, \quad \int \varrho(\boldsymbol{r})\,\boldsymbol{r}\,d\tau \quad \text{and} \quad \int \varrho(\boldsymbol{r})\,\boldsymbol{r}\,\boldsymbol{r}\,d\tau$$

---

[10] E. Clementi, IBM J. Res. Develop. 9, 2 [1965].

Property	Calculated Value NH = 1.905 a. u., HNH = 109° 30′	Experimental Value NH = 1.916 a. u., HNH = 107° 47′
Energy:		
Total electronic energy (SCF)	− 68.2132 a. u.	—
Repulsion of nuclei	11.9864 a. u.	—
Total molecular energy (SCF)	− 56.2268 a. u.	—
Total molecular energy		− 56.5645 a. u.[11]
Energy of separated atoms	—	− 56.1090 a. u.[11]
Energy of sep. atoms (SCF)	− 55.9009 a. u.[10]	—
Dissociation energy	—	0.4555 a. u.
Dissociation energy (SCF)	0.3259 a. u.	—
Ionization potentials: ε_1	0.3859 a. u. (= 10.50 ev)	(11.0 ± 0.02) ev[11] (spectra) (10.25 ± 0.10) ev (photoionization) (10.42 ± 0.05) ev (electron impact)
ε_2	0.5968 a. u. (= 16.24 ev)	(17.0 ± 0.05) ev (spectra) (15.31 ± 0.04) ev (electron impact)
Moments: Dipole	0.5477 a. u. (= 1.3922 × 10^{-18} e.s.u.)	1.46 × 10^{-18} e.s.u.[12]
Quadrupole	− 0.2007 a. u. (= − 0.270 × 10^{-26} e.s.u.)	—
Proton affinity:		
Total molecular energy of NH_4^+	—	− 56.857 a. u.[13] (NH = 1.96 a. u., HNH = 109° 30′)
Total molecular energy of NH_4^+ (S.C.F.)	− 56.5216 a. u.	—
Proton affinity of NH_3	0.295 a. u.	0.277 a. u.[14] (lower limit) 0.362 a. u.[15] (upper limit)

Table 2. Properties of NH_3.

and are respectively the charge, the dipole moment and the quadrupole moment. For calculating these quantities, the origin has been transferred to the nitrogen atom and coordinate axis chosen as shown in Fig. 2.

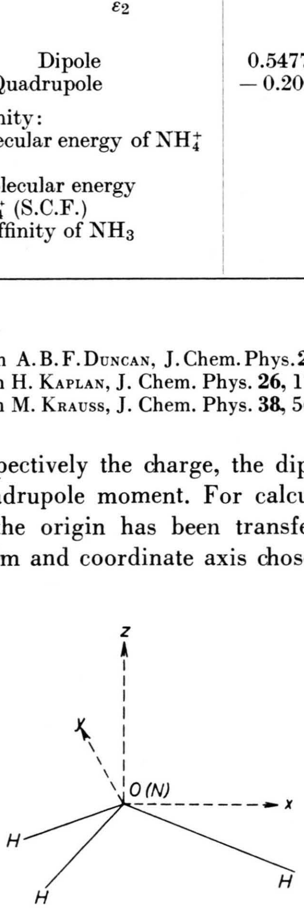

Fig. 2. The coordinate system for calculating moments. The xy plane is parallel to the HHH plane.

For such a choice of the reference axes, the dipole moment is the expectation value of z and its value has been calculated to be 0.5477 a.u. ($= -1.3922 \times 10^{-18}$ e.s.u.) and is in the z direction (Fig. 2).

Following HIRSCHFELDER et al.[16] we define quadrupole moment as the expectation value of $(3\,x^2 - r^2)$ and two other similar expressions with y and z. Such a choice has the advantage that the quadrupole moment tensor is traceless and its off diagonal elements vanish. We have only one independent element Q_{zz} which completely characterizes the quadrupole moment tensor. The calculated value of Q_{zz} is -0.2007 a.u. ($= -0.270 \times 10^{-26}$ e.s.u.).

d) The Proton Affinity of NH_3

The proton affinity of NH_3 is defined as the difference in energies between NH_3 and NH_4^+. A calculation for NH_4^+ has been made for the same configuration as that of NH_3, by placing a proton at the origin in Fig. 1. The calculated energy of NH_4^+ is -56.5216 a.u., so that the proton affinity of NH_3 is calculated to be 0.295 a.u. (= 186 kcal/mole).

V. Conclusions

It has been shown how numerical integration procedures may be used which $(\varphi\varphi : \varphi\varphi)$ integrals can

---

[11] Quoted from A. B. F. DUNCAN, J. Chem. Phys. **27**, 423 [1957].

[12] Quoted from H. KAPLAN, J. Chem. Phys. **26**, 1704 [1957].

[13] Quoted from M. KRAUSS, J. Chem. Phys. **38**, 564 [1963].

[14] F. W. LAMPE and F. FIELD, Tetrahedron **7**, 189 [1959].

[15] D. M. BISHOP, Theor. Chim. Acta **1**, 410 [1963].

[16] J. O. HIRSCHFELDER, C. F. CURTISS, and R. B. BIRD, Molecular Theory of Gases and Liquids, J. Wiley & Sons, New York 1954.

be evaluated directly without expanding each in terms of constituent functions. This makes it possible to introduce the characteristic of accumulative accuracy, which enables computations to be carried on to any desired degree of accuracy, starting from any previously computed wave functions without having to return to the details of the earlier calculation. As more basis functions are used, the method becomes appreciably better than previous methods (such as the one described in reference [1]) as regards programming and machine time required. The direct integration also involves no difficulty when basis functions of the form

$$P(x, y, z, r) \exp(-a\,r)$$

about any centre in the molecule are used. Perhaps better methods can be devised as regards the particular integration techniques. Exploratory investigations on other point systems are in progress.

Appendix I

Points for Integration Around a Single Centre

The aim is to integrate numerically any function $F(r, \lambda, \varphi)$ which is known to behave approximately as $f(\lambda, \varphi) \exp(-a\,r)$ for large r and which is a smooth continuous function except at the origin. r, ϑ, φ are the polar coordinates but it is convenient for the relations below to use $\lambda = \cos\vartheta$. The element of volume of integration is $r^2\,\mathrm{d}r\,\mathrm{d}\lambda\,\mathrm{d}\vartheta$. The procedure described here is one of the best which was found but other arrangements can be devised for this stage.

In order to treat the infinite range of the variable r this is expressed in terms of an auxiliary variable Q so that Q changes from 0 to 1 as r changes for 0 to ∞. An integration with respect to r can then be expressed as

$$\int_0^\infty f(r)\,\mathrm{d}r = \int_0^1 f(r(Q))\,r'(Q)\,\mathrm{d}Q = \frac{1}{M+1}\sum_{i=1}^{M} f\left(r\left(\frac{i}{M+1}\right)\right) r'\left(\frac{i}{M+1}\right) \tag{27}$$

where r' denotes $\mathrm{d}r/\mathrm{d}Q$. This formula shows the summation used for the numerical integration with respect to Q. It is the simple sum of the function of Q at M equally spaced abscisses. The contribution at $Q=0$ and $Q=1$ are omitted because the functions required in these problems are all zero at these values. This is a formula which is exact if the function concerned could be expanded accurately in Fourier series up to $\exp(2\,\pi\,i\,M\,Q)$. As the result of a number of one dimensional tests, chiefly concerned with transforming the cusp of $\exp(-r)$ to a smooth zero value, the following relation between r and Q was used:

$$r = d\,z^4/(z^3+0.25) \quad \text{where} \quad z = Q^{1/2}(1-Q)^{-1/2}. \tag{28}$$

Here d is a constant conveniently called the scale factor. The accuracy is not critically dependent on d but a value of d about three times the mean spherical radius of the electronic function concerned gives about the optimum scale. If i denotes the number of the Q (or r) values in increasing order as shown in the above formula, a variable can be associated with this so that q increases by 1 for each increase of 2 in i,

$$q = \text{integral part of } (i+1)/2\,.$$

Then the values of λ and φ taken with each value of $Q = i/(M+1)$ are

$$(\pm\lambda_u, \varphi_v) \quad \text{for} \quad u = 1, 2, \ldots, q$$

with $\quad \varphi_v = 2\,\pi\,v/j \quad \text{for} \quad v = 1, 2, \ldots, q$

where $\quad j = 2(q+1-u) \quad \text{or} \quad 3(q+1-u)$

for six dimensional integrals (29)

$$\text{or} \quad j = 4\,q \quad \text{or} \quad 4\,q_{\max}$$

for three dimensional integrals.

The values of λ_u are defined to be the roots of the Legendre polynomial of degree $2\,q$. These are widely tabulated together with the associated weights B which give the correct integral values for any polynomial of degree less than $4\,q$.

Since the φ values are equally spaced the resultant weight which must be assigned to such a (λ_u, φ_v) point is $(2\,\pi\,B_u/j)$. This method as a degenerate form of a procedure which gives the exact answer for any linear combination of spherical harmonics of degree less than $4\,q+1$. In the latter case j would have to be taken as $4\,q$. However the angular space associated with the higher values of u is small and the points are relatively close together, so that the $(q+1-u)$ formulae are an ad-hoc way of economising in this.

The result of all these operations is to give the following formula for the integral of F over all space

$$\int_0^0 \int_{-1}^{+1} \int_0^{2\pi} F(r, \lambda, \varphi)\,r^2\,\mathrm{d}r\,\mathrm{d}\lambda\,\mathrm{d}\varphi = \sum_{i=1}^{M}\sum_{u=-q}^{q}\sum_{\mathrm{I}=a}^{j} F\left[r\left(\frac{i}{M+1}\right), \lambda_u, \frac{2\,\pi\,v}{j}\right] r^2 \cdot r'\left(\frac{i}{M+1}\right)\frac{2\,\pi\,B_u}{j(M+1)}\,. \tag{30}$$

The final tests for the r part of the integration were based on the simultaneous evaluation of the integrals

$$\int_0^\infty r^p \exp(-r)\,\mathrm{d}r \quad \text{for} \quad p = 0, 2, 4, 6\,.$$

Then the correctness of the orthogonality integrals for atomic s, p, d functions were used as the general criterion of quality in the development of the (λ, φ) points.

The results from such grids suggest that full numerical integration can provide results to the general order of chemical accuracy, but it is apparent that very useful contributions might still be made by further investigations for better grid systems.

Appendix II

The total number of points in a grid depends on the formula chosen from those given in (29) and on the number of radial points (that is on the value of $i_{\max}$) used. The grids of points for different alternatives, using a unit scale factor have been computed and punched on cards by a program and these form part of the input for succeeding programs. The integral programs carry out the appropriate change of scale. The results of each program which are used by the succeeding one are punched out on cards. This interprogram compatibility has given the sequence of programs flexibility in use; if desired they can be made completely automatic.

In accordance with the method described in section II there are two grids of points, with different scale factors, centred on the N atom and one grid each centred on the H atoms. The values of the scale factors for the particular V_s zones specified in section II were taken as

$$d_1 = 0.44775; \quad d_2 = 1.53846; \quad d_3 = d_4 = d_5 = 2.5 .$$

The number of points per grid varied between 60 and 180 for the calculation of 6 dimensional integrals and between 300 and 2000 for the 3 dimensional integrals. The grid is called fine if 180 points per grid for 6 D integrals and 700 or more points per grid for 3 D integrals are used. Grids with lesser number of points are coarse. The time for each iteration, using a coarse grid varied between half an hour and an hour and a half; for fine grids between two and four hours. The wave function shown in Table 1, with 23 basis functions required about four hours, with a fine grid.

When accumulating integrals, the value itself becomes much larger than the individual addends, consequently because of the shifting to line up the decimal points there is a loss of significant digits from the right hand end of the addends. As the sum grows increasingly larger the resulting truncation for the remaining addends become more extensive. Thus an increase in the number of integration points beyond a certain point produces results which are actually less accurate than more accurate. By a simple programming technique this error has been reduced. This consists in allotting three registers for each accumulated number and accumulating numbers between 0.0 and 0.99, 1.0 and 9.9, and 10.0 and 99.99 in separate registers and adding them together. There does not appear to be much difference between this method and that of adding the contributions for each 100 points of integration and accumulating them. The latter method was adopted eventually since it requires less machine time and storage space.

Acknowledgements

The author wishes to thank Dr. S. F. Boys for having introduced him to molecular quantum mechanics and taught him the efficient use of digital computers. He is indebted to Prof. Dr. L. Biermann whose kindness and hospitality enabled him to come to the Max-Planck-Institut. Several conversations with Frau Dr. E. Trefftz are also acknowledged. Thanks are also due to the Staff of the Rechenzentrum of the Institut für Plasmaphysik at Garching for facilities to use the IBM 7090 computer on which these computations were performed.