PHYSICAL REVIEW A VOLUME 2, NUMBER 4 OCTOBER 1970

Protonic Structure of Molecules. II. Methodology, Center-of-Mass Transformation, and the Structure of Methane, Ammonia, and Water*

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(Received 18 May 1970)

A center-of-mass–transformed Hamiltonian is used to study the molecular structure of methane, ammonia, and water, where the protons as well as the electrons are described by Slater determinants of one-particle Slater functions. The matrix elements of the Hamiltonian are given for a wave function constructed from a product between a sum of Slater determinants for the electrons and a sum of Slater determinants for the protons. The ground states of the protons were the ^5S multiplet of the sp^3 configuration at -39.13764 hartrees for methane, the ^4P multiplet of the sp^2 configuration at -55.44522 hartrees for ammonia, and the ^3P multiplet of the sp configuration at -75.50005 hartrees for water. The energies of the other protonic multiplets of the above configurations are given also, as are the energies of the protonic multiplet of the s^2p^2 and p^4 configurations in methane, of the s^2p and p^3 configurations in ammonia, and of the s^2 and p^2 configurations in water. The errors in the wave functions are discussed.

INTRODUCTION

In the Paper I of this series,[1] we discussed the results of a variational solution to Schrödinger's equation for the ammonia molecule. In that calculation, the nitrogen atom was fixed at the origin of the coordinate system, and both the protons and electrons moved about it. The Hamiltonian, therefore, included the kinetic energy operators of the protons as well as those of the electrons. We used a product-type wave function made up of Slater-type orbitals (STO's) to find an approximate solution to the problem. We feel that the results of that calculation were novel enough to warrant further study.

In this paper we will discuss in detail the methodology of molecular quantum mechanics using the Hamiltonian

$$\sum_i\left(\frac{-1}{2m_i}\nabla_i^2+\sum_{j>i}\frac{q_iq_j}{r_{ij}}\right) , \tag{1}$$

where m_i and q_i are the mass and charge of the ith particle, and the summation indices run over all the particles of the molecule. We will not use the Born-Oppenheimer perturbation expansion of the Hamiltonian.

CENTER-OF-MASS TRANSFORMATION

We wish to transform Eq. (1) into c.m. coordinates. We will do this by setting the origin of the relative coordinates on one of the particles which we will call particle a. Our relative coordinates will be defined by

$$\vec{R}_i=\vec{r}_i-\vec{r}_a , \quad i\neq a \tag{2}$$

where $\vec{r}_a$ is the position vector particle a. The remaining three coordinates are given by the vector to the center of mass, which is

$$\vec{R}=\sum_i m_i\vec{r}_i+m_a\vec{r}_a/\sum_i m_i+m_a , \tag{3}$$

where now the sum over i excludes $i=a$. The transformed Hamiltonian is

$$H'=-\frac{1}{2M}\nabla_R^2-\sum_{i\neq a}\frac{1}{2\mu_i}\nabla_i^2-\frac{1}{m_a}\left(\sum_i\sum_{j>i}\nabla_i\cdot\nabla_j\right)+V, \tag{4}$$

i and $j\neq a$, where the i and j indices now refer to the relative coordinates defined by Eq. (2):

$$M=\sum_i m_i+m_a , \quad \mu_i=m_am_i/(m_a+m_i) . \tag{5}$$

The transformation does not change the potential represented now by V.

Since we will not be concerned with the motion of the center of mass, the Hamiltonian we will use is

$$H=H'-T , \tag{6}$$

where T is the kinetic energy of the center of mass.

If we want to make the cross terms in the kinetic energy as small as possible, the form of Eq. (4) tells us that m_a should be the most massive particle in the molecule. Note that for $m_a\rightarrow\infty$, our Hamiltonian reduces to the Hamiltonian which we used in Paper I. As an example, we consider hydrogen fluoride. The most massive particle in this system is the fluoride nucleus of mass m_f. It also has a proton of mass m_p, and ten electrons of mass m ($m=1$ in our choice of units). The Hamiltonian is

$$H=-\sum_{i=1}^{10}\frac{1}{2\mu_e}\nabla_i^2-\frac{1}{2\mu_p}\nabla_p^2-\frac{1}{m_f}\left[\sum_{i=1}^{10}\nabla_i\cdot\left(\nabla_p+\sum_{j>i}^{10}\nabla_j\right)\right]+V. \tag{7}$$

WAVE FUNCTION AND MATRIX ELEMENTS

A system of particles which interact has a wave function which must be a function of the interparticle distances; but, of course, we do not know how to solve that problem for more than two particles. However, a wave function constructed from products of single-particle functions has been very successful. Although approximate, it can be made as accurate as one likes. We will only deal with this type of wave function. Furthermore, we will restrict our discussion to a system containing only two different types of particles, since the extension to more than two different types is obvious.

The wave function can be written as

$$\Psi = \sum f_a(1) f_b(2) \cdots f_z(x) \quad ,$$

where f's are the single-particle functions and x is the total number of particles. If we are describing n electrons and m protons, we should antisymmetrize the electrons and protons. Consequently, we write

$$\Psi = (n!)^{-1/2} \sum_P (-1)^P P[f_1(1) \cdots f_n(n)] (m!)^{-1/2} \times \sum_Q (-1)^Q Q[g_1(1) \cdots g_m(m)] \quad , \tag{8}$$

where we have distinguished the electron functions from the proton functions by using the symbol f for the former and g for the latter, and P and Q are the usual permutation operators. If, instead of protons, we were describing m bosons, our wave function would be written as

$$\Psi = F(m_1! m_2! \cdots m_z! m!)^{-1/2} \times \sum_Q Q[g_1(1) \cdots g_1(m_1) g_2(m_1+1) \cdots \times g_2(m_2) \cdots g_z(m-m_2+1) \cdots g_z(m_z)] \quad , \tag{9}$$

where F represents the antisymmetrized product of electron functions, and $m_1, m_2, \ldots, m_r$ are the number of bosons in each function ($\sum_i m_i = m$). In general, we want our functions which describe the electrons and the protons to be sums of antisymmetrized products, each of which we will call a configuration, i.e.,

$$\Psi = \sum_i C_i F_i \sum_a C_a G_a = \sum_i \sum_a C_{ia} F_i G_a \quad , \tag{10}$$

where F represents an antisymmetrized product of electron functions and G_a represents an antisymmetrized or symmetrized product of fermion or boson functions, respectively.

When we use the variational theorem to obtain an approximate solution to the time-independent Schrödinger equation, we obtain the usual secular equation

$$|H_{\alpha\beta} - E S_{\alpha\beta}| = 0 \, ;$$

but now

$$H_{\alpha\beta} = \int F_i^* G_a^* H F_j G_b \, dV = (ia|H|jb) \quad ,$$

$$S_{\alpha\beta} = \int F_i^* G_a^* F_j G_b \, dV = (ia|jb) \quad ,$$

where the index α is related to i and a through the relation

$$\alpha = a + a_{\max}(i-1) \quad ,$$

and similarly for the β index. In what follows we will restrict ourselves to orthogonal configurations. The overlap integrals are very simple:

$$\int F_i^* G_a^* F_j G_b \, dV = \int F_i^* F_j \, dV_e \int G_a^* G_b \, dV_p = \delta_{ij} \delta_{ab} \, , \tag{11}$$

where dV_e is the product of the electronic volume elements, and dV_p is the product of the protonic volume elements. This result for the overlap integrals holds for G being an antisymmetrized or symmetrized product. We can partition the Hamiltonian in the following way:

$$H = H_e + H_p + H_{ep} \quad , \tag{12}$$

where

$$H_e = \sum_I \left[-\frac{1}{2\mu} \nabla_I^2 - \frac{1}{r_I} + \sum_{J>I} \left(\frac{1}{r_{IJ}} - \frac{1}{m} \nabla_I \cdot \nabla_J \right) \right] , \tag{13}$$

$$H_p = \sum_A \left[-\frac{1}{2\mu_p} \nabla_A^2 + \frac{1}{r_A} + \sum_{B>A} \left(\frac{1}{r_{AB}} - \frac{1}{m} \nabla_A \cdot \nabla_B \right) \right] , \tag{14}$$

$$H_{pe} = -\sum_I \sum_A \left(\frac{1}{m} \nabla_I \cdot \nabla_A + \frac{1}{r_{IA}} \right) \quad , \tag{15}$$

where r_I and r_A are the distances of the electron and proton from the heavy atom of mass m, respectively. A typical matrix element is

$$(ia|H_e + H_p + H_{ep}|jb) = (i|H_e|j)\delta_{ab} + (a|H_p|b)\delta_{ij} + (ia|H_{ep}|jb) \quad , \tag{16}$$

where

$$(i|H_e|j) = \int F_i^* H_e F_j \, dV_e \quad , \tag{17}$$

$$(a|H_p|b) = \int G_a^* H_p G_b \, dV_p \quad , \tag{18}$$

$$(ia|H_{pe}|jb) = \int F_i^* G_a^* H_{pe} F_j G_b \, dV_e \, dV_p \quad . \tag{19}$$

Save for the $\nabla \cdot \nabla'$, the development of Eqs. (17) and (18) into integrals over the one-particle functions can be found elsewhere[2]; therefore, we will treat only those operators. We will begin with the electronic operator:

$$\begin{aligned}(i|\sum_I \sum_{J>I} \nabla_I \cdot \nabla_J |j) &= (n!)^{-1} \int \sum_P (-1)^P \\ &\quad \times P[f_{i1}(1) \cdots f_{in}(n)]^* \sum_I \sum_{J>I} \nabla_I \cdot \nabla_J \\ &\quad \times \sum_Q (-1)^Q Q[f_{j1}(1) \cdots f_{jn}(n)] \, dV_1 \cdots dV_n \\ &= \int [f_{i1}(1) \cdots f_{in}(n)]^* \sum_I \sum_{J>I} \nabla_I \cdot \nabla_J [f_{j1}(1) \cdots \\ &\quad \times f_{jI}(I) f_{jJ}(J) \cdots - f_{j1}(1) \cdots f_{jI}(J) f_{jJ}(I) \cdots] \\ &\quad \times dV_1 \cdots dV_I \, dV_J \cdots dV_n \quad .\end{aligned}$$

This integral will have a different development for four different cases:

(a) If $i=j$, then the integral equals

$$\sum_I \sum_{J>I} \left[\int f_I^*(1)\, \nabla_1 f_I(1)\, dV_1 \cdot \int f_J^*(2)\, \nabla_2 f_J(2)\, dV_2 - \int f_I^*(1)\, \nabla_1 f_J(1)\, dV_1 \cdot \int f_J^*(2)\, \nabla_2 f_I(2)\, dV_2 \right] . \tag{20}$$

(b) If $i \neq j$ and F_i and F_j differ by only one function, with f_k in F_i, where f_r is in F_j, then the integral equals

$$\sum_{I\neq k} \left[\int f_I^*(1)\, \nabla_1 f_I(1)\, dV_1 \cdot \int f_k^*(2)\, \nabla_2 f_r(2)\, dV_2 - \int f_I^*(1)\, \nabla_1 f_r(1)\, dV_1 \cdot \int f_k^*(2)\, \nabla_2 f_I(2)\, dV_2 \right] . \tag{21}$$

(c) If $i \neq j$ and F_i and F_j differ by two functions with f_k and f_l in F_i, where f_r and f_s are in F_j, the integral equals simply

$$\int f_k^*(1)\, \nabla_1 f_r(1)\, dV_1 \cdot \int f_l^*(2)\, \nabla_2 f_s(2)\, dV_2 - \int f_k^*(1)\, \nabla_1 f_s(1)\, dV_1 \cdot \int f_l^*(1)\, \nabla_2 f_r(2)\, dV_2 . \tag{22}$$

(d) If F_i and F_j differ by more than two functions the integral vanishes. The treatment of the protonic operator is exactly the same. All that needs to be done is to change i to a, j to b, f to g, I to A, and J to B.

It will be easier to consider the two parts of H_{pe} separately, beginning with

$$\begin{aligned}(ia|\sum_I \sum_A \nabla_I \cdot \nabla_A |jb) &= \int F_i^* G_a^* \sum_I \sum_A \nabla_I \cdot \nabla_A F_j G_b\, dV \\ &= \int F_i^* \sum_I \nabla_I F_j\, dV_e \cdot \int G_A^* \sum_A \nabla_A G_B\, dV_p \\ &= \int f_{i1}^*(1) \cdots f_{in}^*(n) \sum_I \nabla_I f_{j1}(1) \cdots f_{jn}(n)\, dV_e \\ &\quad \cdot \int g_{a1}^*(1) \cdots g_{am}^*(m) \sum_A \nabla_A g_{b1}(1) \cdots g_{bm}(m)\, dV_p .\end{aligned}$$

For this integral we need to consider only cases (a) and (b) since both the electronic part and the protonic part will vanish for cases (c) and (d); but we will have four different developments because we can have case (a) electronic–case (a) protonic, case (a) electronic–case (b) protonic, case (b) electronic–case (a) protonic, and case (b) electronic–case (b) protonic. The four results are as follows:

For case (a) electronic–case (a) protonic, the integral equals

$$\sum_I \int f_I^*(1)\, \nabla_{e1} f_I(1)\, dV_{e1} \cdot \sum_A \int g_A^*(1)\, \nabla_{p1} g_A(1)\, dV_{p1} . \tag{23}$$

For case (a) electronic–case (b) protonic, the integral equals

$$\int g_r^*(1)\, \nabla_{p1} g_s(1)\, dV_{p1} \cdot \sum_I \int f_I^*(1)\, \nabla_{e1} f_I(1)\, dV_{e1} . \tag{24}$$

For case (b) electronic–case (a) protonic, the integral equals

$$\int f_k^*(1)\, \nabla_{e1} f_l(1)\, dV_{e1} \cdot \sum_A \int g_A^*(1)\, \nabla_{p1} g_A(1)\, dV_{p1} . \tag{25}$$

For case (b) electronic–case (b) protonic, the integral equals

$$\int f_k^*(1)\, \nabla_{e1} f_l(1)\, dV_{e1} \cdot \int g_r^*(1)\, \nabla_{p1} g_s(1)\, dV_{p1} . \tag{26}$$

We have left to consider the $1/r_{IA}$ operator. This integral is

$$\left(ia\left|\sum_I \sum_A \frac{1}{r_{IA}}\right|jb\right) = \int F_i^* G_a^* \sum_I \sum_A \frac{1}{r_{IA}} F_j G_b\, dV_e\, dV_p . \tag{27}$$

We will have for this integral four results analogous to the four which we found for the integral involving the $\nabla_I \cdot \nabla_A$ operators. Again cases (c) and (d) need not be considered since the integral vanishes for these cases.

For case (a) electronic–case (a) protonic, the integral equals

$$\sum_I \sum_A \int f_I^*(e) f_I(e)\, (1/r_{ep})\, g_A^*(p) g_A(p)\, dV_e\, dV_p . \tag{28}$$

For case (a) electronic–case (b) protonic, the integral equals

$$\sum_I \int f_I^*(e) f_I(e)\, (1/r_{ep})\, g_r^*(p) g_s(p)\, dV_e\, dVp . \tag{29}$$

For case (b) electronic–case (a) protonic, the integral equals

$$\sum_A \int f_k^*(e) f_l(e)\, (1/r_{ep})\, g_A^*(p) g_A(p)\, dV_e\, dV_p . \tag{30}$$

For case (b) electronic–case (b) protonic, the integral equals

$$\int f_k^*(e) f_l(e)\, (1/r_{ep})\, g_r^*(p) g_s(p)\, dV_e\, dV_p . \tag{31}$$

The development of Eq. (18) into integrals over the one-particle functions when G_a and G_b are symmetric products is given in a separate paper.[3]

WAVE FUNCTIONS FOR CH_4, NH_3, and H_2O

All the basis functions were of the form

$$f \text{ or } g = (2z)^{n+1/2} [\Gamma(2n+1)]^{-1/2} r^{n-1} e^{-zr} Y_{lm}(\theta, \phi) ,$$

where n and z are the orbital parameters. Since noninteger n's were used, the basis functions are not labeled 1s, 2s, etc., but rather s, s' where the letter denotes the angular momentum, i.e., $s = 0$, $p = 1$, etc.

The electronic part of the wave functions of methane, ammonia, and water was a ^1S, $s^2 s'^2 p^6$ configuration. The orbital parameters are given in Table I. The orbital parameters for the protonic part of the wave function are given in Table II along with $(n-1)/z$, the maximum of the function, and the experimental "internuclear distance". One can see that our agreement with the experimentally determined maximums (i.e., internuclear dis-

TABLE I. Electronic orbital parameters for methane, ammonia, and water.

Function	CH_4		NH_3		H_2O	
	n	z	n	z	n	z
s	0.9857	5.5875	0.9885	6.5835	0.9903	7.5748
s'	2.0623	1.4772	1.9972	1.7728	2.0004	2.1371
p	1.5835	0.9943	1.5162	1.1823	1.5005	1.4401

tances) is not bad.

For methane, we used the sp^3 configuration with the ^5S, ^3D, ^3P, ^3S, ^1D, ^1P multiplets, the s^2p^2 configuration with the ^3P, ^1D, ^1S multiplets, and the p^4 configuration with the ^3P, ^1D, ^1S multiplets. For ammonia we used the sp^2 configuration with the ^4P, ^2D, ^2P, ^2S multiplets, the s^2p configuration with the ^2P multiplet, and the p^3 configuration with the ^4S, ^2D, ^2P multiplets. For water we used the sp configuration with the ^3P, ^1P multiplets, the s^2 configuration with the ^1S multiplet, and the p^2 configuration with the ^3P, ^1D, ^1S multiplets.

EFFECTS OF CENTER-OF-MASS TRANSFORMATION

The masses of the electron and proton which we used are 9.1091×10^{-28} and 1.67252×10^{-24} g, respectively.[4] In our Hamiltonian, all masses are in electron mass units. From the two numbers given above, we get 1836.1 for the mass of the proton in our units. The value of an amu in electron mass units is 1822.8, which was found by dividing 1836.1 by 1.00727663 – the mass of the proton in amu.[4] The masses of the other nuclei were found by multiplying 1822.8 by their weighted average atomic weight as given on a periodic chart based on carbon 12 and subtracting for the electrons. Table III gives these data.

Two calculations were done with each molecule. Water will be used as the prototype in the discussion which follows. In the first calculation, the mass of the oxygen nucleus was infinite. Hence, the reduced electronic mass was 1, the reduced protonic mass was equal to the protonic mass, and the third term of Eq. (4) was zero. The second calculation differed from the first because we used the correct mass for the oxygen nucleus and the c.m.-transformed Hamiltonian. The results of these calculations are given in Tables IV and V.

In Table IV we have given the values of the sum of the kinetic and one-particle potential energies. Note that the increase in energy due to the reduced electronic mass is 0.00254 hartrees (i.e., the sum of the differences between calculations one and two multiplied by two since the orbitals are doubly occupied) while the increase in energy due to the reduced protonic mass is 0.000602 hartrees.

Table V gives the integrals which involve the $(1/m_a)\,\nabla_i\cdot\nabla_j$ operator. Note that here also the largest contributions to the energy come from the electronic coordinates. Finally, from Table VI we see that the difference in total energies between calculations one and two is 0.005 hartrees. This is a negligible quantity when compared with the total energy; but it is not negligible when compared to the bond energies since it amounts to about 3% of an OH bond. It is about as large as a hydrogen bond and as large as or larger than barriers to inversion or barriers to internal rotation.

In Table VI we give the ground-state energies of H_2O, NH_3, and CH_4 for the infinitely massive central atom Hamiltonian and for the c.m.-transformed Hamiltonian. Note that even though H_2O has the largest difference between the two calculations, that difference is the smallest percentage of the ground-state energy, as would be expected, since oxygen has the most massive nucleus. Table VII summarizes the c.m.-transformation effects for all three molecules. It is interesting that the total kinetic energy given in the third row is nearly constant for the three molecules even though the kinetic energy per particle decreases from H_2O to CH_4. For whatever they are worth, we give some interesting ratios in Table VIII, where we see that the ratio of the masses or charges of the central nucleus to that of the oxygen nucleus is nearly the same as the change in electronic kinetic energy between the two calculations. We find the same ratios again in the column where we took the ratios of the $\nabla\cdot\nabla'$ integrals of the molecules to the $\nabla\cdot\nabla'$ integrals for H_2O. The last column shows that the ratio of the change in kinetic energy to the $\nabla\cdot\nabla'$ integrals is nearly constant for these molecules.

It is tempting to make use of the ratios of Table VIII to estimate the $(\nabla\cdot\nabla')$ term for other mole-

TABLE II. Protonic orbital parameters for methane, ammonia, and water.

	CH_4	NH_3	H_2O
n	125.27	124.58	115.30
z	56.889	62.913	62.792
$\frac{(n-1)}{z}$	2.184	1.964	1.820
R_e[a]	2.067	1.916	1.810

[a] G. Hertzberg, *Infrared and Raman Spectra* (Van Nostrand, New York, 1950).

TABLE III. Nuclear, reduced protonic, and reduced electronic masses (mass of electron = 1.0).

Mass	C	N	O
nucleus	21 888.0	25 524.0	29 156.0
μ_p	1 694.0	1 712.9	1 727.3
μ_e	0.999 95	0.999 96	0.999 97

cules, since from the table we find that

$$(\nabla\cdot\nabla')_i \approx (m_j/m_{\mathrm{O}})(\nabla\cdot\nabla')_{\mathrm{H_2O}} \ ,$$

where i refers to a molecule and j to the mass of the nucleus at the origin of the relative coordinate system; we can get a similar relation for the kinetic energy:

$$\frac{T_i}{m_j} \approx \frac{m_j}{m_{\mathrm{O}}}\left(\frac{T_{\mathrm{H_2O}}}{m_{\mathrm{O}}}\right) \ .$$

We will pursue the validity of these relations as we complete calculations for more molecules and for atoms.

CALCULATED PROTONIC SPECTRA

The protonic energy levels of CH_4, NH_3, and H_2O are given in Table IX. These levels differ from those given in Refs. 1 and 5 because there we used a nonspherical electronic charge distribution for NH_3 and H_2O, a set of hybrid protonic orbitals for H_2O and NH_3 which resulted essentially in a p^2 configuration for H_2O, and a fixed central nucleus. Here we used a spherical electronic charge distribution for all calculations; we did not use hybrid orbitals, and we used the c.m.-transformed Hamiltonian.

A nonspherical electronic charge distribution does give a lower ground-state energy for NH_3. The improvement, however, may be accidental because our electronic functions are by no means the best. We will pursue this question when we have better electronic functions. The difference in the ground-state energy is small: 0.0002 hartrees. In water, however, the spherical electronic charge distribution gives a better energy by 0.0009 hartrees for the ^3P multiplet of the sp protonic configuration.

We note from Table IX that for methane the ^3P multiplet of the s^2p^2 configuration is much higher in energy than the ^5S multiplet of the sp^3 configuration. The opposite is found for electrons in carbon. The reason for this is that electrons have sufficient kinetic energy to pair while protons do not. We can state as a general rule that the lowest multiplet of a configuration which has paired protons will be higher than the lowest multiplet of a configuration which has no paired protons. We also find from Table IX that the rules governing the order of the multiplets of a given configuration are the same for protons as for electrons. These rules are as follows: The state of highest multiplicity lies lowest, and for states with the same multiplicity, the state with highest angular momentum lies lowest.

Since the protonic transitions are governed by the same selection rules as the electrons,[6] the transitions which can occur are exactly those which one would expect if the spectra of Table IX were electronic.

CONCLUSION

If the results of the calculations described in this paper and in Refs. 1 and 5 are correct, it will be necessary for quantum chemistry to modify its views on molecular structure. We hope in this section to examine some of the errors in these calculations.

The most obvious source of error is the lack of correlation in the wave function of the motion among the electrons and protons. We can, however, get estimates of this error which we will call electronic error, protonic error, and protonic-electronic error, by comparing the ground-state energies which we got using the fixed-central-nucleus (FCN) approximation with the ground-state energies got from the fixed-nuclear-framework (FNF) approximation using the same electronic function for both calculations. The assumption on which our estimates depend is that the error in the electronic part of our wave function is the same as the error in the electronic function of the FNF calculation.

TABLE IV. Effects of center-of-mass transformation on one-particle integrals in H_2O.

	Electronic functions in integral[a]			Protonic functions in integral		
Calc.[b]	s, s	s', s'[c]	p, p[d]	s, s	p, p[d]	Total energy
1	−31.935 59	−6.779 598	−5.778 373	4.361 449	4.361 614	−75.494 986
2	−31.934 60	−6.779 509	−5.778 309	4.361 726	4.361 896	−75.500 045

[a] Values are for the sum of the kinetic plus one-particle potential energy. The orbital parameters are given in Table I.

[b] Calculation 1 used an infinitely massive oxygen nucleus. Calculation 2 used the c.m.-transformed Hamiltonian.

[c] s' function is the Schmidt orthorgonalized second electronic function of Table I.

[d] In this calculation $p_x = p_y = p_z$.

The ground-state energies of the FCN and FNF calculations are given in Ref. 5. We will use the FNF energies for HF, H_2O, NH_3, and CH_4 and the FCN energies for NH_3 and CH_4 given there. The correct FCN ground-state energy of H_2O is -75.4941 hartrees and the FCN ground-state energy of HF without the approximate c. m.-transformation used in Ref. 5 is -99.6484 hartrees.

Let E' be the true ground-state energy of the FCN Hamiltonian for HF. The calculated energy E_c' is related to E' as

$$E' = E_c' + E_e' + E_{pe} ,$$

where E_e' is the electronic error and E_{pe} is the protonic-electronic error. If E is the true ground-

TABLE VI. Ground-state energies of H_2O, NH_3, and CH_4.

Calculation[a]	H_2O	NH_3	CH_4
1	−75.494 94	−55.441 10	−39.134 37
2	−75.500 05	−55.445 22	−39.137 64
Δ_{21}	−0.005 09	− 0.004 12	− 0.003 27
%	0.006 6	0.007 4	0.008 2

[a] Calculation 1 used an infinitely massive central atom. Calculation 2 used for the c. m.-transformed Hamiltonian. The symbol Δ_{21} stands for the difference between calculation 2 and calculation 1. The last row, labeled %, is the percent of the energy of calculation 2 which Δ_{21} represents.

TABLE V. $(1/m_a)\ \nabla_i \cdot \nabla_j$ integrals in H_2O.

Integral[a]	Electronic-electronic	Protonic-protonic	Protonic-electronic
(ss/ss)	0.002 006 682 6	0.000 010 172 2	0.000 142 871 9
(ss/ss')	−0.000 506 105 8		−0.000 036 033 7
$(ss/s's)$	−0.000 002 466 1		−0.000 000 175 6
$(ss/s's')$	0.000 308 539 7		0.000 021 967 4
(ss/sp_z)	0.000 273 525 1	0.000 013 837 7	0.000 019 474 5
$(ss/s'p_z)$	0.000 305 919 6		0.000 021 780 9
(ss/pp)	0.000 251 789 4	0.000 010 172 2	0.000 017 926 9
(ss/p_xp_y)	0.000 292 008 9	0.000 011 983 8	0.000 021 119 6
(ss/p_yp_x)	−0.000 292 008 9	−0.000 011 983 8	−0.000 021 119 6
$(s's/ss')$	−0.000 077 816 9		
$(s's/s's)$	−0.000 000 379 2		
$(s's/s's)$	0.000 047 439 9		
$(s's'/sp_z)$	0.000 042 056 2		
$(s's/s'p_z)$	0.000 047 037 0		
$(s's/pp)$	0.000 038 714 2		
$(s's'/p_xp_y)$	0.000 045 609 0		
$(s's'/p_yp_x)$	−0.000 045 609 0		
(sp_z/sp_z)	0.000 037 283 4	0.000 018 824 2	0.000 026 492 1
$(sp_z/s'p_z)$	0.000 041 699 0		0.000 029 629 6
(sp_z/pp)	0.000 034 320 7	0.000 013 837 7	0.000 024 386 9
(sp_z/p_xp_y)	0.000 040 433 1	0.000 011 983 8	0.000 028 730 1
(sp_z/p_yp_x)	−0.000 040 433 1	−0.000 011 983 8	−0.000 028 730 1
$(s'p_z/s'p_z)$	0.000 046 637 6		
$(s'p_z/pp)$	0.000 038 385 4		
$(s'p_z/p_xp_y)$	0.000 045 221 7		
$(s'p_z/p_yp_x)$	−0.000 045 221 7		
(pp/pp)	0.000 031 593 4	0.000 010 172 2	0.000 017 926 9
(pp/p_xp_y)	0.000 037 220 1	0.000 011 983 8	0.000 021 119 6
(pp/p_yp_x)	−0.000 037 220 1	−0.000 011 983 8	−0.000 021 119 6
(p_xp_y/p_xp_y)	0.000 032 484 9	0.000 014 118 1	0.000 024 881 0
(p_xp_y/p_yp_x)	−0.000 032 484 9	−0.000 014 118 1	−0.000 024 881 0
(p_xp_y/ss)			0.000 168 316 9
(p_xp_y/ss')			−0.000 042 451 2
$(p_xp_y/s's)$			−0.000 000 206 9
$(p_xp_y/s's)$			0.000 025 879 8
(p_xp_y/sp_z)			0.000 022 942 8
$(p_xp_y/s'p_z)$			0.000 025 660 0
(p_xp_y/pp)			0.000 021 119 6

[a] The symbol (f_1f_2/f_3f_4) represents the integral $\int\int f_1^*(1) f_3^*(2)(1/m_a)\, \nabla_1 \cdot \nabla_2 f_2(1) f_4(2)\, dV_1 dV_2$. In the protonic-electronic integrals, particle 1 is the proton and particle 2 is the electron.

TABLE VII. Effects of center-of-mass transformation in H_2O, NH_3, and CH_4.

Quantity[a]	H_2O	NH_3	CH_4
Δ_e	0.002 52	0.002 14	0.001 76
Δ_p	0.000 67	0.000 94	0.001 21
Δ_p	0.003 19	0.003 08	0.002 97
$(\nabla\cdot\nabla')$	-0.008 28	-0.007 20	-0.006 24

[a] Δ_e represents the difference in total electronic kinetic energy between calculations 2 and 1. Δ_p is the same as Δ_e for the protons. Δ is the sum of Δ_e and Δ_p. $(\nabla\cdot\nabla')$ represents $(1/m_a)\ \Sigma_i\Sigma_{j>i}\ \nabla_i\cdot\nabla_j$ obtained by subtracting Δ from Δ_{21} of Table VI.

state energy of the FNF Hamiltonian for HF and E_c is the calculated energy, then

$$E=E_c+E_e\ ,$$

where E_e is the electronic error. By assumption

$$E_e=E_e'\ ,\qquad \Delta E=\Delta E_c-E_{pe}\ ,$$

where

$$\Delta E=E-E'\ ,\ \Delta E_c=E_c-E_c'\ ;$$

or

$$E_{pe}=\Delta E_c-\Delta E\ .$$

The ΔE is equal to the kinetic energy of the protons. For this kinetic energy we will use the value of the protonic kinetic energy from our calculation, 0.0053 hartrees. One could perhaps use the experimental vibrational plus rotational ground-state energies, but then one would have to remove the center-of-mass effects which are included in the experimental results. The end result of the procedure would probably result in as great an error as the error in our kinetic energy. Also, the true kinetic energy of the protons for the FCN Hamiltonian must be greater than or equal to that which we have already got because we certainly do not expect an increase in the protonic wavelength as the protonic function is improved. Therefore, the use of our calculated protonic kinetic energy at least gives us the direction of the error. ΔE_c is -0.0167 hartrees, so

$$E_{pe}=-0.0114\ \text{hartrees,}$$

or, since there are ten possible proton-electron pairs,

$$e_{pe}=\tfrac{1}{10}E_{pe}=-0.001\,14 \qquad (32)$$

is the proton-electron error per pair. We realize, of course, that the proton interaction with the s electrons is less than with the p electrons and that e_{pe} is only an average.

The relation between E' and E_c' for water in the FCN calculation is

TABLE IX. Calculated protonic energy levels of CH_4, NH_3, and H_2O in hartrees.

Molecule	Configuration[a]	Multiplet	Energy
CH_4	sp^3	^5S	-39.137 64
		^3D	-38.863 41
		^3P	-38.863 38
		^3S	-38.592 23
		^1D	-38.590 70
		^1P	-38.590 67
	s^2p^2	^3P	-38.848 21
		^1D	-38.756 26
		^1S	-38.710 31
	p^4	^3P	-38.728 45
		^1D	-38.636 51
		^1S	-38.590 59
NH_3	sp^2	^4P	-55.445 22
		^2D	-55.191 49
		^2P	-55.140 43
		^2S	-54.990 58
	p^3	^4S	-55.312 22
		^2D	-55.159 00
		^2P	-55.158 97
	s^2p	^2P	-55.208 68
H_2O	sp	^3P	-75.500 05
		^1P	-75.174 50
	p^2	^3P	-75.428 33
		^1D	-75.318 84
		^1S	-75.264 13
	s^2	^1S	-75.318 84

[a] Each configuration was diagonalized separately.

TABLE VIII. Some interesting ratios.

	$y=O$			$y=H_2O$	
x	$m_x/m_y=z_x/z_y$	x	Δ_{ex}/Δ_{ey}	$(\nabla\cdot\nabla')_x/\nabla\cdot\nabla')_y$	$\Delta_x/(\nabla\cdot\nabla')_x$
O	1.00	H_2O	1.00	1.00	0.26
N	0.88	NH_3	0.85	0.87	0.23
C	0.75	CH_4	0.70	0.75	0.21

$$E' = E_c' + E_e' + E_{pe} + E_p \ ,$$

where E_p is the protonic error, and for the FNF calculation, the relation is

$$E = E_c + E_e \ .$$

Again, by assumption,

$$E_e' = E_p \ ,$$

$$E_p = \Delta E_c - \Delta E - E_{pe}$$

$$= \Delta E_c - \Delta E - 20 e_{pe} \ ,$$

since there are 20 possible proton-electron pairs in water. When we substitute the values for ΔE_c, ΔE, and from Eq. (1), e_{pe}, we get

$$E_p = -0.0154 \text{ hartrees.}$$

Thus, our estimated error per proton in H_2O is

$$e_p = \tfrac{1}{2} E_p = -0.0077 \text{ hartrees.}$$

The estimated error per proton for NH_3 and CH_4 are found in the same way. These data are summarized in Table X.

TABLE X. Estimated errors in CH_4, NH_3, H_2O, and HF.

	CH_4	NH_3	H_2O	HF
ΔE_c	-0.3713	-0.2365	-0.0477	-0.0167
ΔE	-0.0145	-0.0133	-0.0095	-0.0053
E_{pe}	-0.0456	-0.0342	-0.0228	-0.0114
e_p	-0.0778	-0.0630	-0.0077	

The values of E_p should not be confused with correlation energy, since that quantity is defined as

$$E_{\mathrm{corr}} = E - E_{\mathrm{HF}} \ ,$$

where E is the true ground-state energy and E_{HF} is the Hartree-Fock ground-state energy. Our E_p is necessarily a larger negative number than E_{corr} since we centainly do not have the Hartree-Fock solution. An atomic minimal-basis calculation for fluorine gives an energy of -98.94211 hartrees[7] while the Hartree-Fock solution gives an energy of -99.40928 hartrees.[8] The difference is -0.46717 hartrees, which when added to the correlation energy, -0.324 hartrees, gives a total of -0.791 hartrees for what we would call the electronic error. This electronic error is what would correspond to our protonic error, since we also use a minimal basis. When we divide -0.791 by 9, we get -0.0879 for the electronic error per electron in fluorine from a minimal-basis calculation while the correlation error per electron is -0.036 hartrees. In oxygen, we find -0.065 hartrees for the error per electron and 0.032 hartrees for the correlation energy per electron. In helium we get -0.0281 hartrees for the error per electron and -0.0210 hartrees for the correlation per electron, and in lithium we get -0.0199 hartrees for the error per electron and -0.0131 hartrees for the correlation per electron. Therefore, we might expect that the correlation per proton is something of the order of 50–80% of the values given in Table X. One might infer from the results given above for fluorine and oxygen that the correlation energy for protons could be less than for electrons, but since the electrons are paired and the protons are not, such an inference would be incorrect. Nor is it true that our many-configuration wave functions correct for much of the correlation because the 20-configuration solution for CH_4 was only -0.0007 hartrees better than the single-configuration wave function.

Another obvious question which can be raised is the following: What about the "vibrational and rotational" spectra? We are not prepared to go into detail to answer this question at this time, but we hope that the next paper in this series will be devoted to this question. What we said in the first part of this series concerning the vibrational and rotational structure we now believe to be incorrect. The "vibrational and rotational" structure probably arises from a much more obvious source. The orbital parameter n is related to the principal quantum number. For n's as large as are necessary for the protons, the energy separation between two n's, say 100 and 101, must be small. It is along these lines that we expect to interpret the vibrational and rotational structure. [One of us (I. L. T.) received this suggestion from Snyder of Bell Telephone Laboratories.]

We come finally to the experimental verification of the protonic spectra. As we have shown in Ref. 6, the selection rules and intensities of the protonic transitions for excitations with light are the same as those found for electrons. Therefore, it would be difficult to assign unambigiously a transition to a protonic excitation. What one needs is a source of energy which would excite protons but not electrons. As Hulett of Oak Ridge National Laboratory pointed out, neutrons do just that. We hope that through the efforts of Mook, also of Oak Ridge National Laboratory, the necessary experiments will be done in the near future. We also hope to use the "photoprotonic" effect to verify the protonic spectra. This effect should exist and should be completely analogous to the photoelectric effect.

ACKNOWLEDGMENTS

We acknowledge the benefit we received from discussions with E. Guth and H. C. Schwindler of Oak Ridge National Laboratory.

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*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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PHYSICAL REVIEW A VOLUME 2, NUMBER 4 OCTOBER 1970

Atomic Bethe-Goldstone Calculations of the Hyperfine Structure of B(^2P)

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(Received 7 April 1970)

A variational generalization of Brueckner's theory has been applied to the calculation of hyperfine parameters for the ^2P ground state of atomic boron. The computational method makes use of a hierarchy of *n*th-order (or *n*-particle) variational Bethe-Goldstone equations defined in terms of configurational excitations of a Hartree-Fock reference state. Hyperfine parameters are computed as the sum of net increments defined at each level of the hierarchy. Orbital basis sets are extrapolated to practical completeness for each one- and two-particle net increment. Three-particle net increments are found to be small but not negligible. Computed magnetic hyperfine constants are within roughly 1% of experiment. The electric field gradient is computed, and its relative accuracy is estimated from that of the magnetic hyperfine constants. Combined with experimental quadrupole coupling constants, this implies values of the nuclear quadrupole moments $Q(\mathrm{B}^{10}) = 0.08472\,(56)$ b and $Q(\mathrm{B}^{11}) = 0.04065\,(26)$ b, with the indicated precision.

I. INTRODUCTION

The hyperfine structure of atomic energy levels arises from the interaction between nuclear moments and the static electric and magnetic fields produced at the nucleus by the atomic electrons. A nuclear magnetic moment $\vec{\mu}$ interacts with the electrons through an effective Hamiltonian

$$h a_J \vec{\mathrm{I}} \circ \vec{\mathrm{J}} \quad , \tag{1}$$

where $\vec{\mathrm{I}}$ is the nuclear spin and $\vec{\mathrm{J}}$ is the electronic total angular momentum. If both $\vec{\mathrm{I}}$ and $\vec{\mathrm{J}}$ are expressed in atomic units (angular momentum divided by $\hbar$) then a_J is in frequency units (energy divided by h). There are three contributions to a_J of different tensorial character.[1] For light atoms, when the electronic wave function has definite quantum numbers L and S, the Fermi contact, spin-dipolar, and orbital contributions to a_J, in the state $J = L + S$, can be expressed in the form, respectively,[1,2]

$$\begin{aligned} a_{J,c} &= \gamma_{JI} \tfrac{1}{6} g_e X_c \quad , \\ a_{J,\mathrm{dip}} &= \gamma_{JI} \tfrac{1}{2} g_e X_{\mathrm{dip}} \quad , \\ a_{J,\mathrm{orb}} &= \gamma_{JI} X_{\mathrm{orb}} \quad , \end{aligned} \tag{2}$$

such that

$$a_J = a_{J,c} + a_{J,\mathrm{dip}} + a_{J,\mathrm{orb}} \quad .$$

Here we have

$$g_e = 2.00232 \quad , \tag{3}$$

$$\gamma_{JI} = G_{en} \mu_I / JI \quad , \tag{4}$$

where μ_I is the nuclear magnetic moment in nuclear magnetons, I is the nuclear spin quantum number, and

$$G_{en} = 95.4129 \text{ MHz} \quad , \tag{5}$$

using recently tabulated values of fundamental constants.[3]

The dimensionless constants X_c, X_{dip}, and X_{orb} in Eqs. (2) are operator mean values computed for the electronic wave function of the state with $M_L = L$, $M_S = S$, and $M_J = L + S = J$:

$$\begin{aligned} \hbar a_0^{-3} X_c &= [\vec{\mathrm{s}}\delta] = \langle 8\pi \textstyle\sum_i s_{zi}\, \delta(\vec{\mathrm{r}}_i) \rangle_{LS} \quad , \\ \hbar a_0^{-3} X_{\mathrm{dip}} &= [\vec{\mathrm{s}}\, \overleftrightarrow{\mathrm{C}}^{(2)}] = \langle 2 \textstyle\sum_i s_{zi}\, r_i^{-3}\, C_0^{(2)}(\theta_i) \rangle_{LS} \quad , \\ \hbar a_0^{-3} X_{\mathrm{orb}} &= [\vec{\mathrm{l}}\,] = \langle \textstyle\sum_i r_i^{-3}\, l_{zi} \rangle_{LS} \quad . \end{aligned} \tag{6}$$