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Protonic Structure of Molecules. I. Ammonia Molecules*

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The ammonia molecule is treated in this calculation with the nitrogen fixed and with the electrons and protons described by Slater orbitals. The Hamiltonian includes the kinetic-energy operators of the protons. One minimal basis configuration was used for the electrons, and twenty configurations involving six orthogonal spin orbitals constructed from the s, p_x, p_y, and p_z basis orbitals were used for the protons. Proton delocalization was found to be significant, and the kinetic energies of the protons were found to be about 3 kcal/mole. The calculation yielded a protonic spectrum similar to the electronic spectrum. A ground-state energy of -55.44 hartrees was obtained.

INTRODUCTION

The Hamiltonian usually used in molecular quantum mechanics is, in hartrees,

$$H' = \sum_i \left(-\frac{1}{2}\Delta_i - \sum_a \frac{Z_a}{r_{ai}}\right) + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{a<b} \frac{Z_a Z_b}{r_{ab}} , \tag{1}$$

where the i and j indices refer to the electrons, the a and b refer to the nuclei, and Z_a represents the nuclear charge. When a molecular problem is solved using the variational theorem, the wave function is often given the following form:

$$\psi' = (n!)^{-1/2} \sum_P (-1)^P P[\phi_1(1)\phi_2(2)\cdots\phi_n(n)] , \tag{2}$$

where the ϕ_i's are one-electron functions. The sum is over all distinct permutations among the n electrons, and $(-1)^P$ is $+1$ if there is an even number of pair exchanges, -1 if it involves an odd number.

The Hamiltonian of Eq. (1) assumes that the nuclei are fixed. However, there is no reason to assume this, since the kinetic-energy operator for the nuclei can be included in the Hamiltonian by changing Eq. (1) to

$$H = \sum_a \frac{1}{2m_a}\Delta_a - \sum_i \frac{1}{2}\Delta_i - \sum_a \sum_i \frac{Z_a}{r_{ai}} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{a<b} \frac{Z_a Z_b}{r_{ab}} , \tag{3}$$

and Eq. (2) to

$$\psi = \Phi \text{ (electrons) } \Omega \text{ (nuclei)}, \tag{4}$$

where $\Phi = (n_e!)^{-1/2} \sum_P (-1)^P P[\phi_1(1)\cdots\phi_{n_e}(n_e)]$,

and, for nuclei of half-integer spin,

$$\Omega = \prod_a (n_a!)^{-1/2} \sum_P (-1)^P P[\eta_{a1}(1)\cdots\eta_{an_a}(n_a)] ,$$

where the η_a's are one-nucleus functions, n_e is the number of electrons, n_a is the number of a nuclei, and m_a is the mass of the a nucleus.

The Hamiltonian Eq. (3) has a higher ground-state energy than that of Eq. (2) since the kinetic energy is a positive quantity, but the ground-state energy of neither Hamiltonian corresponds to the ground-state energy of a given molecule because both are approximate. However, H should have a ground-state energy closer to that of a given molecule than the ground state of H'. There is also a computational advantage in using Eqs. (3) and (4) rather than (1) and (2) because multicenter molecular problems can be reduced to one-center problems.

In order to test the usefulness of H and ψ, a calculation was done on the ammonia molecule with the nitrogen atom fixed. The Hamiltonian, therefore, was

$$H = \sum_{a=1}^{3} \left(-\frac{1}{2m}\Delta_a + \frac{7}{r_a} + \sum_{b>a}^{3} \frac{1}{r_{ab}}\right) + \sum_{i=1}^{10} \left(-\frac{1}{2}\Delta_i - \frac{7}{r_i} + \sum_{j>i}^{10} \frac{1}{r_{ij}}\right) - \sum_{a=1}^{3} \sum_{i=1}^{10} \frac{1}{r_{ai}}, \tag{5}$$

where r_a is the distance of the a proton from the nitrogen, r_i is the distance of the i electron from the nitrogen, and m is the mass of the proton. The η's and ϕ's of Eq. (4) were taken to be one-proton Slater functions and one-electron Slater functions centered on the nitrogen, i.e.,

$$\phi \text{ or } \eta = (2\xi)^{n+1/2}[(2n)!]^{-1/2} r^{n-1} e^{-\xi r} Y_{lm}(\theta, \phi) . \tag{6}$$

Since the 10 electrons form a closed shell, a single determinant using a basis set of s, s', p_x, p_y, and p_z Slater functions was used to describe the electrons. The protons, however, do not form a closed shell. Furthermore, experimental evidence suggests that the protonic structure would be best described by three orthogonal orbitals. In order to span three dimensions, the set of s, p_x, p_y, and p_z Slater functions were used to construct three orthogonal proton orbitals.

There are 20 different ways of arranging three protons in the six spin orbitals. Since a protonic spectrum would have been interesting, it was decided to include all 20 spin configurations. Therefore, the wave function used had the following form:

$$\psi = \Phi \sum_{i=1}^{20} \Omega_i , \tag{7}$$

where the Ω_i's have the form

$$\Omega = \sum_P (-1)^P P[\eta_k(1)\eta_l(2)\eta_m(3)] ,$$

where the η's are three of the six spin orbitals. The wave function was optimized with respect to all the orbital parameters and the mixing coefficients of the proton functions. The 1s and 2s electron functions were Schmidt orthogonalized.

RESULTS AND DISCUSSION

The best sets of parameters are given in the first and third lines of Table I. Two things are worth noting in this table. One is that the electronic parameters of this calculation are very similar to the electronic parameters obtained by Rutledge and Saturno,[1] which are given on the second line. This result supports the Born-Oppenheimer approximation. The other is the size of the protonic parameters. Table II gives the mixing coefficients of the proton orbitals. Note that the p_z coefficient is zero. Since the p_z coefficient is zero and the s, p_x, and p_y are orthogonal, the use of the sp-type hybrid orbitals does not change the energy or the wave function. However, it was decided to leave the coefficients as they stand to make the interpretation of the wave function more conventional.

Now consider Fig. 1 where the square of the p_x

TABLE I. Orbital parameters of the electron and proton Slater functions.

	s		s'		P_x		P_y		P_z	
Type	n	ξ	n	ξ	n	ξ	n	ξ	n	ξ
Electron	0.9880	6.581	1.996	1.772	1.516	1.181	1.516	1.181	1.506	1.188
Rutledge and Saturno (Ref. 1)	0.9880	6.580	2.021	1.799	1.506	1.231	1.506	1.231	1.545	1.210
Proton	125.2	63.19	•••	•••	125.2	63.19	125.2	63.19	124.7	63.06

TABLE II. Mixing coefficients of the proton orbitals.

Orthogonal	Coefficients			
orbital	s	p_x	p_y	p_z
1	$1/\sqrt{3}$	$2/\sqrt{6}$	0.0	0.0
2	$1/\sqrt{3}$	$-1/\sqrt{6}$	$1/\sqrt{2}$	0.0
3	$1/\sqrt{3}$	$-1/\sqrt{6}$	$-1/\sqrt{2}$	0.0

electron function and the square of the proton function which lies along the x axis are plotted. The plot of the electron function is as would be expected. Its maximum lies in the bond closer to the nitrogen than to the proton. Examination of the proton function shows that its maximum is nearly at the equilibrium internuclear distance and that it is not a δ function. In fact, the proton has a reasonable probability of being anywhere from 1.8 to 2.1 bohrs. However, this proton delocalization is not nearly as striking as that shown in Fig. 2. This figure gives the square of the three proton orbitals in the x-y plane at $r = 1.980$ bohrs as the angle ϕ goes from 0 to 2π. Note that each maximum is separated by 120 deg as one would expect. Figure 3 gives the square of the proton orbital as a function of the angle θ at $r = 1.980$ bohrs and $\phi = 0$, 120, or 240 deg. Note again the smeared protonic charge. The delocalization above and below the x-y plane includes the equilibrium positions of the protons which are used in the fixed nuclei approximation to describe the spectrum of ammonia.

The eigenfunctions and eigenvalues are given in Table III. Note that the eigenvalues are almost all equally spaced apart by about 0.1 hartree. This spectrum is clearly not the vibrational or rotational spectrum. However, it is interesting to note the similarity in Fig. 4 between the calculated spectrum and the experimental spectrum. Are some of the observed lines protonic excitations? The vibrational structure will probably arise from the proton-spin-orbit and/or proton-orbit-electron-spin interactions. A future publication will consider this possibility. Vibrations and rotations could still be considered in this model since the nitrogen is considered fixed. But a true c.m.-transformed Hamiltonian, which we are investigating with simpler molecules, such as

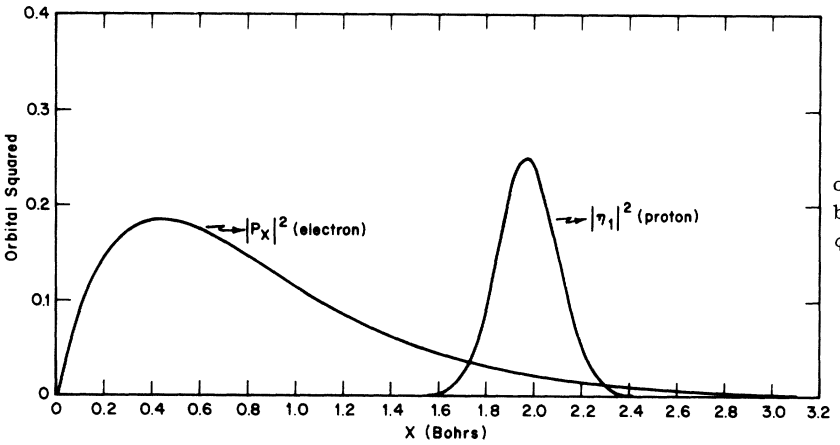

FIG. 1. Square of the p_x electron orbital and the square of the proton orbital directed along the x axis at $\theta = \frac{1}{2}\pi$, $\phi = 0$, and $x = 0$–3.2 bohrs.

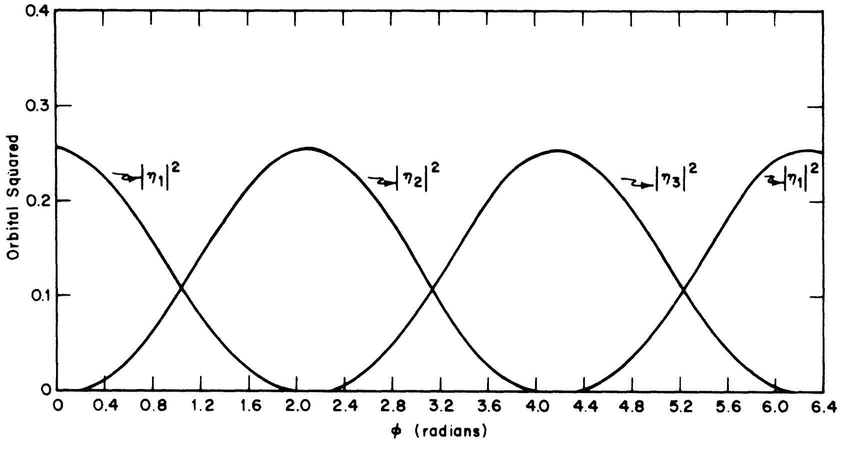

FIG. 2. Square of the three proton orbitals in the x-y plane at $r = 1.980$ bohrs, $\theta = \frac{1}{2}\pi$, and $\phi = 0$–2π.

H_2, would not give the classical picture of a vibrating rotating molecule. The evidence in favor of this statement may be seen in Sharma's work on the excitonic and positronium molecules.[2]

This calculation shows that the kinetic energy of a proton is 4.49×10^{-3} hartrees and of a p electron 1.25 hartrees. The proton kinetic energies amount to about 3% of the bond energy of ammonia. Furthermore, these kinetic energies imply momentums of 4.06 and 1.58 (in atomic units) for a proton and a p electron, respectively. Therefore, the de Broglie wavelength of a proton is about one-third that of an electron in the ammonia molecule.

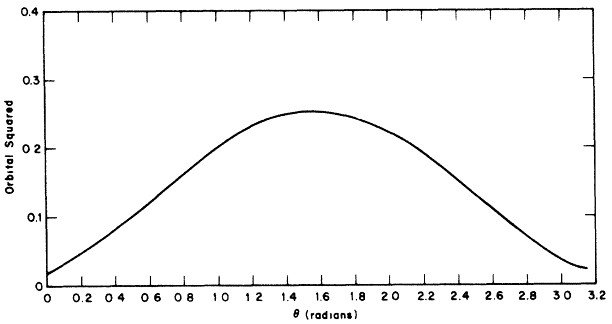

FIG. 3. Square of a proton orbital at $r=1.980$ bohrs, $\phi=0$, $\frac{2}{3}\pi$, or $\frac{4}{3}\pi$, and $\theta=0-\pi$.

TABLE III. Protonic eigenvalues and eigenfunctions of ammonia.

Eigenvalues[a] (hartrees)		Eigenfunctions[b]
−54.98668	(20)	0.40825[(11′2) − (11′2′) − (123′) + (133′) + (12′3) − (233′)]
	(19)	0.40825[(11′2′) − (11′3) − (1′22′) + (1′33′) + (22′3) − (2′33′)]
−54.99475	(18)	−0.52365(11′2′) + 0.51659(11′3) − 0.04712(122′) − 0.05449(123′) − 0.05177(12′3) + 0.06155(133′) + 0.1063(1′23) + 0.4621(22′3) − 0.47188(233′)
	(17)	−0.52365(11′2′) + 0.51659(11′3′) − 0.04712(1′22′) + 0.05449(1′2′3) + 0.05177(1′23′) + 0.06155(1′33′) − 0.1063(12′3′) + 0.4621(22′3′) − 0.47188(2′33′)
	(16)	0.23126(11′2) + 0.24662(11′3) − 0.57069(122′) + 0.09124(123′) − 0.09281(12′3) − 0.56912(133′) − 0.00157(1′23)
	(15)	0.23126(11′2′) + 0.24662(11′3′) − 0.57069(1′22′) − 0.09124(1′2′3) + 0.09281(1′23′) − 0.56912(1′33′) − 0.00157(12′3′)
−55.08547	(14)	−0.40825[(11′2) + (11′3) + (122′) + (133′) + (22′3) + (233′)]
	(13)	+0.40825[(11′2′) + (11′3′) + (1′22′) + (1′33′) + (22′3′) + (2′33′)]
−55.18763	(12)	0.46753[(12′3) + (233′) − (11′2)] − 0.28597[(11′3) + (123′) − (22′3)] − 0.18156[(122′) + (1′23) − (133′)]
	(11)	0.46753[(11′2′) + (1′23′) − (2′33′)] − 0.28597[(1′2′3) + (22′3′) − (11′3′)] − 0.18156[(12′3′) + (1′33′) − (1′22′)]
	(10)	0.43504[(133′) − (122′) − (1′23)] + 0.37476[(133′) + (123′) − (22′3)] + 0.06282[(12′3) + (233′) − (11′2)]
	(9)	0.43504[(12′3′) + (1′33′) − (1′22)] + 0.37476[(11′3′) − (1′2′3) − (12′3′)] + 0.06282[(2′33′) − (11′2′) − (1′23′)]
−55.3149	(8)	−0.32943(11′2′) − 0.33247(11′3′) + 0.01177(12′3′) + 0.09791(1′22′) + 0.56399(1′23′) − 0.57576(1′2′3) + 0.08613(1′33′) + 0.24330(22′3′) + 0.23456(233′)
	(7)	0.32943(11′2) + 0.33247(11′3) + 0.01177(1′23) − 0.09791(1′22′) + 0.56399(12′3) − 0.57576(123′) − 0.08613(133′) − 0.24330(22′3) − 0.23456(233′)
	(6)	0.09074(11′2) − 0.07890(11′3) + 0.32737(122′) + 0.31882(123′) + 0.33921(12′3) − 0.33066(133′) − 0.65804(1′23) + 0.23993(22′3) − 0.24848(233′)
	(5)	0.09074(11′2′) − 0.07890(11′3′) + 0.32737(1′22′) − 0.31882(1′2′3) − 0.33921(1′23′) − 0.33066(1′33′) + 0.65804(12′3′) + 0.23993(22′3′) − 0.24848(2′33′)
−55.44135	(4)	1.0 (123)
	(3)	1.0 (1′2′3′)
	(2)	0.57735[(123′) + (12′3) + (1′23)]
	(1)	−0.57735[(12′3′) + (1′23′) + (1′2′3)]

[a] Rutledge and Saturno got −55.68 hartrees using the fixed nuclei approximation (see Ref. 1).

[b] The symbol (11′2) represents a Slater determinant with a proton of spin $\frac{1}{2}$ in orbital one, a proton of spin $-\frac{1}{2}$ in orbital one, and a proton in orbital two with spin $\frac{1}{2}$. The other symbols have a similar meaning.

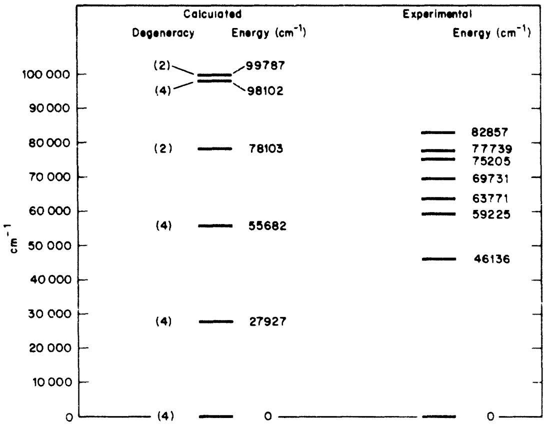

FIG. 4. Calculated protonic spectrum and experimental spectrum from G. Herzberg, Electronic Spectra of Polyatomic Molecules (D. van Nostrand Co., Inc., New York, 1966), p. 609.

CONCLUSION

This calculation gives a molecular structure for the ammonia molecule which is radically different from the usual one. The molecule appears as an inner ellipsoid of electronic charge surrounded by a belt of protonic charge. A spectrum of protonic states emerges similar to the electronic states. The vibrational and rotational states do not appear and must be due to terms not included in the Hamiltonian.

Other parts in this series on protonic structure will consider the molecules CH_4, H_2O, HF, B_2H_6, C_2H_6, LiH, and H_2, the problem of vibrational and rotational states, hydrogen bonding, proton tunneling, and rearrangement scattering involving protons. We also hope to improve our results by including more than a minimal basis for the electronic configurations, larger basis sets for the protonic configurations, and excited electronic states. Since this calculation indicates that there is a protonic spectrum similar to the electronic, we are investigating the possibility that there may exist protonic bands in solid hydrides.

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[1] R. M. Rutledge and A. F. Saturno, J. Chem. Phys. 44, 977 (1966).

[2] R. R. Sharma, Phys. Rev. 170, 770 (1968); 171, 36 (1968).