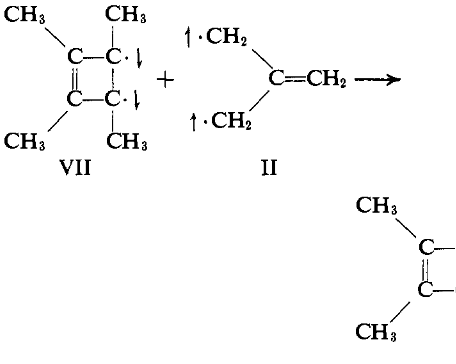
VII II VIII

added to a singlet tetramethylcyclobutadiene, the resulting triplet adduct would not have been expected to give only a single cross-coupling product, but rather a number of monocyclic compounds *via* reduction, or internal or external disproportionation. Therefore the cross-coupling product VIII was formed in a one-step process involving the simultaneous formation of both bonds. The analogous bicyclic product[16] was obtained using *cis*-3,4-dichlorocyclobutene[17] and 2-chloromethyl-3-chloropropene, thus implicating a triplet cyclobutadiene intermediate.

The combined observations indicate that trimethylenemethane was produced and that is exists in a relatively stable triplet state, as predicted by theoretical calculations and in agreement with the esr results.

(16) 3-Methylenebicyclo[3.2.0]hept-6-ene was identified on the basis of the following spectral evidence: the mass spectrum had a parent peak at m/e 106 corresponding to the formula C_8H_{10}; the infrared spectrum showed absorption bands at 3.29 (vinyl hydrogen), 5.93 (cyclobutene double bond), 6.00, and 11.15 μ (terminal methylene group); the nmr spectrum consisted of a singlet at 5.91 ppm and multiplets at 4.83, 3.20, and 2.12 ppm in a ratio of 1:1:1:2, respectively.

(17) A generous sample of *cis*-3,4-dichlorocyclobutene was furnished by Professor C. D. Nenitzescu.

(18) This work was supported by the National Science Foundation.

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Received February 18, 1967

A Simple Floating Localized Orbital Model of Molecular Structure

Sir:

Most molecules have an even number of electrons which are generally paired off to create a ground state which is a spectroscopic singlet. For such molecules and states the following quantum mechanical model is proposed.

Let there be a minimal set of n floating localized orbitals φ_i which are, in general, nonorthogonal and real, and let each one be occupied by a pair of electrons with opposing spin. The $2n$-electron wave function can then be written as a single normalized Slater determinant

$$\psi = |\varphi_1(1)\bar{\varphi}_1(2)\varphi_2(3)\bar{\varphi}_2(4)\ldots\varphi_n(2n-1)\bar{\varphi}_n(2n)| \quad [1/(\sqrt{(2n)!}\ \det S)]$$

where the bars over certain orbitals indicate β spin as opposed to α for the others, and det S is the determinant of the orbital overlap matrix S with elements

$$S_{ij} = \int \varphi_i^*\varphi_j\,\mathrm{d}v$$

Given the set of orbitals and the appropriate nonrelativistic Hamiltonian operator H, the mean energy E is calculated according to a formula adapted from one derived by Löwdin[1]

$$E = \int\psi^*H\psi\,\mathrm{d}\tau = 2\sum_{i,j}(i/j)T_{ij} + \sum_{i,j,k,l}(ij/kl)(2T_{ij}T_{kl} - T_{il}T_{jk})$$

where

$$(i/j) = \int \varphi_i^*h\varphi_j\,\mathrm{d}v$$

are the kinetic and potential energy integrals with the one-electron operator h, and

$$(ij/kl) = \int\varphi_i^*(1)\varphi_j(1)\varphi_k^*(2)\varphi_l(2)(1/r_{12})\,\mathrm{d}v(1)\mathrm{d}v(2)$$

are the electron repulsion energy integrals. T_{ij}'s are elements of the reciprocal orbital overlap matrix

$$T = S^{-1}$$

For a given set of nuclear coordinates E is minimized, according to the variation method, by a variation in parameters defining the orbitals. This will generate a potential energy surface. If a "full minimization" of E with respect to nuclear coordinates as well as orbital parameters is carried out, then the equilibrium configurations of the molecule will be predicted. The calculation is strictly *ab initio* with no semiempirical parameters.

In this simple model the orbitals are taken to be floating spherical Gaussian functions[2]

$$\varphi_i = (2/\pi\rho_i^2)^{3/4}\exp[-(r_i/\rho_i)^2]$$

where r_i is the radial distance from the center of the orbital and ρ_i is an "orbital radius" parameter which defines a sphere which includes about 74% of the orbital charge density. For each orbital the coordinates of the center as well as the orbital radius are parameters to be varied.

Minimization of E with respect to all parameters will automatically lead to a result which will satisfy both the virial theorem and the Hellmann–Feynman theorem.[3]

Table I presents typical results for a series of diatomic and polyatomic molecules by the full minimization procedure.

The calculated energies are, of course, well above experimental values since no electron correlation is included other than that between electrons of like spin due to the antisymmetrization inherent in the determinantal wave function. Also the energies must be higher than those of Hartree–Fock calculations since the latter are by definition the values obtained by all possible variations of the orbitals in a single determinantal wave function. Because the total energies are crude, it would be expected that dissociation energies would be unsatisfactory and no attempt has been made to calculate them.

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(1) P.-O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).

(2) S. F. Boys, *Proc. Roy. Soc.* (London), **A200**, 542 (1950), introduction of gaussian orbitals; H. Preuss, *Z. Naturforsch.*, **11a**, 823 (1956); **19a**, 1335 (1964); **20a**, 18, 21, 1290 (1965); J. L. Whitten, *J. Chem. Phys.*, **39**, 349 (1963); **44**, 359 (1966); J. L. Whitten and L. C. Allen, *ibid.*, **43**, S170 (1965), use of off-center spherical Gaussian "pure" or "lobe" functions to simulate nonspherical atomic orbitals.

(3) A. C. Hurley, *Proc. Roy. Soc.* (London), **A226**, 170, 176, 193 (1954).

Table I. Calculated Energies and Bond Lengths According to the Floating Localized Orbital Model with Spherical Gaussian Functions

Molecules	Negative total energy (hartrees) This work	Negative total energy (hartrees) Hartree–Fock		Bond length, A Calcd	Bond length, A Obsd[h]
H_2	0.956	1.1336[a]		0.780	0.741
LiH	6.572	7.9851[b]		1.712	1.595
Li_2	12.282	14.8718[c]		2.807	2.672
HF	84.635	100.0580[d] (min at $R = 0.920$ A)		0.779	0.917
BeH_2					
linear	13.214			1.412	
BH_3					
planar D_{3h}	22.297	26.2358[e] (min at $R = 1.16$ A)		1.245	1.19 (av)
CH_4					
tetrahedral	33.992	39.8660[f] (min at $R = 1.10$ A)		1.115	1.093
NH_3					
pyramidal C_{3v}	47.568	55.9748[f] (min. at $R = 1.04$ A)		1.008	1.012
planar D_{3h}	47.141			1.489	. . .
H_2O					
angular C_{2v}	64.290	75.9224[f] (min at $R = 0.963$ A)		0.880	0.957
linear	64.203			1.621	. . .
C_2H_2			C≡C	1.210	1.205
linear, sym	64.684	76.7916[g]			
			C=H	1.073	1.059
C_2H_4			C=C	1.350	1.337
planar, D_{2h}	65.836	78.0012[g]			
			C—H	1.104	1.085

[a] W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 205 (1960). [b] D. D. Ebbing, *J. Chem. Phys.*, **36**, 1361 (1962). [c] P. E. Cade and A. C. Wahl, quoted by G. Das, *ibid.*, **46**, 1568 (1967). [d] E. Clementi, *ibid.*, **36**, 33 (1962). [d] B. D. Joshi, *ibid.*, **46**, 875 (1967). [f] R. Moccia, *ibid.*, **37**, 910 (1962); **40**, 2164, 2176, 2186 (1964). [g] R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *ibid.*, **46**, 2029 (1967). [h] Observed values are taken from L. E. Sutton, Ed., "Interatomic Distances," Special Publication No. 18, The Chemical Society, London, 1965.

The calculated bond lengths are surprisingly close to the experimental values, on the average within 4.4%. Considering the crudeness of the model no such direct quantitative similarity would be expected. However, the model should give general trends which certainly are present.

Bond angles are not as successfully calculated although NH_3 and H_2O are properly predicted to be pyramidal and bent, respectively. The angles are: H-N-H, 88.0° (obsd 106.6°); and H-O-H, 89.5° (obsd 104.5°).

Dipole moments (Debyes) are calculated to be: LiH, 6.56 (obsd 5.882); HF, 1.66 (obsd 1.98); H_2O, 1.92 (obsd 1.84); and NH_3, 1.71 (obsd 1.46).

LiH is a simple example which shows how the orbital parameters behave. One orbital turns out to have a small "radius," ρ, equal to 0.707 bohr and is located 0.0076 bohr from the Li nucleus on the side opposite from the proton. This can be considered an inner-shell Li orbital. The other orbital has a radius of 2.44 bohrs and is located about 89% of the way from Li to H. The bond could therefore be interpreted to be predominantly ionic.

This model has a simpler relation to the original electron pairing and shared pair concepts of Lewis[4] than does the quantum mechanical valence bond method since the present model uses only one orbital per electron pair bond instead of two. It is also related to molecular orbital theory through the use of a single determinantal wave function. Localized molecular orbitals have been discussed particularly by Lennard-Jones and co-workers[5] and by Edmiston and Ruedenberg.[6]

This model constitutes an extension of the Kimball–Neumark[7] spherical Gaussian orbital model which was applied by Neumark to the simple systems He and H_2. The "charge cloud" model of Kimball[7] which conceives of uniformly charged spheres for electron pairs resembles the present model but does not allow for overlap of the spheres and is only pseudo-quantum mechanical. Likewise the tangent-sphere model of Bent[8] and related ideas of King,[9] although giving considerable qualitative insight into molecular structure, are not sufficient for quantitative calculations. Details of the calculations and additional results will be published elsewhere.

Acknowledgment. This research has been supported by a grant from the National Science Foundation to Northwestern University.

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Received March 29, 1967

The Coordination Number of Aluminum(III) in Liquid Ammonia[1]

Sir:

Various nmr techniques[2–4] have been used to determine hydration numbers of ions in aqueous solutions. We have attempted to extend these methods to liquid ammonia and wish to report the results for Al(III) solutions. The method used was to determine the area under the ^{14}N nmr absorption line in the species $Al(NH_3)_x^{3+}$ after broadening the solvent line beyond detection by addition of Cu(II). The exchange of bound ammonia in the Cu(II) complex is very rapid.[5] The area measurements were calibrated using various known species.

[1] Report No. RLO-1031-6 of work supported by the U. S. Atomic Energy Commission.

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