Table IV. Thermodynamic Quantities for the Dissociation of Glycine and Some Substituted Glycines at 25°

	pK	$\Delta H°$, cal mol^{-1}	$\Delta S°$, cal K^{-1} mol^{-1}	$\Delta C_p°$, cal K^{-1} mol^{-1}
	First Dissociation Step			
Glycine[a]	2.350	953	−7.6	−34
Tricine	2.023	1405	−4.6	−46
	Second Dissociation Step			
Glycine[a]	9.780	10550	−9.4	−12
Bicine[b]	8.333	6279	−17.1	1
Tricine	8.135	7520	−12.0	−12
N-Methylglycine[c] (sarcosine)	10.200	9681	−14.2	−3
N,*N*-Dimethylglycine[c]	9.940	7654	−19.8	+14

[a] Reference 4. [b] Reference 24. [c] S. P. Datta and A. K. Grzybowski, *Trans. Faraday Soc.*, **54**, 1179, 1188 (1958).

The alterations in acidic strength for both dissociation steps brought about by N substitution in glycine are probably to be attributed both to inductive and steric effects.[23] The change in pK_2 is more pronounced than in pK_1, probably because the substituent is located adjacent to the protonated nitrogen but relatively remote from the carboxyl group. A similar enhancement of acidic strength is apparent in the pK_2 of "bicine," that is, *N*,*N*-bis(2-hydroxyethyl)glycine.[24] On the contrary, N-methyl substitution lowers the acidic strength of the protonated nitrogen group.

Hydroxymethyl or hydroxyethyl substitution usually lowers the value of $\Delta H°$ for isoelectric dissociation processes, in addition to lowering pK.[23,25] The first dissociation step of glycine corresponds closely with this charge type, provided the zwitterion behaves as an uncharged molecule. It appears, however, that $\Delta H°$ increases with substitution of the tris(hydroxymethyl)-methyl group into glycine. The changes of entropy likewise show no consistent pattern.

It is apparent that the value of $\Delta C_p°$ found for the second dissociation of tricine (−12 cal K^{-1} mol^{-1} at 25°) is very close to that (−11.7 cal K^{-1} mol^{-1}) for glycine found by King[4] and to the average value (−14 cal K^{-1} mol^{-1}) found for other amino acids,[5,26] but it differs by 13 cal K^{-1} mol^{-1} from that found for bicine.[24] Although charge type appears to be the primary factor determining the magnitude of $\Delta C_p°$ for a dissociation process,[27] there is mounting evidence[24] that nonelectrostatic effects involving changes in water structure often play an important role. These interactions are of such a complexity that any attempt to account for the thermodynamic quantities associated with the dissociation of these zwitterionic species is still necessarily speculative.

The authors thank Mr. T. K. Ghosh for assistance with the computer programming.

Supplementary Material Available. Tables of the emf of cells I and II will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-8231.

---

(23) M. Paabo and R. G. Bates, *J. Phys. Chem.*, 74, 702 (1970).

(24) S. P. Datta, A. K. Grzybowski, and R. G. Bates, *J. Phys. Chem.*, **68**, 275 (1964).

(25) B. A. Timimi and D. H. Everett, *J. Chem. Soc. B*, 1380 (1968).

(26) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids, and Peptides," Reinhold, New York, N. Y., 1943, p 80.

(27) Reference 5, Chapter 15.

Consideration of the VSEPR Model by a Localized Molecular Orbital Study of the Geometry of H_2O

Conrad A. Naleway* and Maurice E. Schwartz

Contribution from the Department of Chemistry and the Radiation Laboratory,[1] *University of Notre Dame, Notre Dame, Indiana 46556.*

Received March 12, 1973

Abstract: The H_2O molecule is studied as a function of HOH angle by the *ab initio* LCAO–SCF–MO method with extended basis sets. The symmetry adapted canonical MO's are transformed into a set of localized MO's (LMO's) by the minimum exchange energy criterion. A variety of energy interactions among these LMO's are considered with a view toward analyzing the VSEPR model for determining molecular geometry. In general, good agreement is obtained between the results and VSEPR. Other orbital characteristics such as charge density and orbital directionality are also considered, and an examination is made of alternate criteria which may be useful in determining molecular geometry.

One of the more useful concepts in predicting and understanding molecular shape is the localized electron pair, especially as formulated in the valence shell electron pair repulsion theory (VSEPR).[2] The fundamental principle of this theory is that electron pairs in the valence level of a central atom orient themselves about the nucleus and inner shell so that the net

---

(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-881.

(2) (a) R. J. Gillespie, *Angew. Chem., Int. Ed. Engl.*, **6**, 819 (1967); (b) R. J. Gillespie, *J. Chem. Educ.*, **47**, 19 (1970).

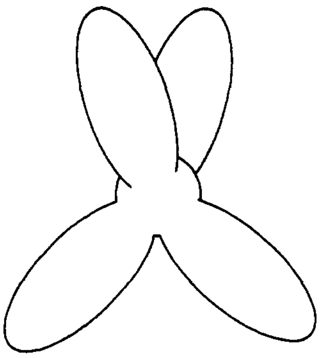

Figure 1. A schematic representation of the nearly tetrahedral localized orbital set within the water molecule.

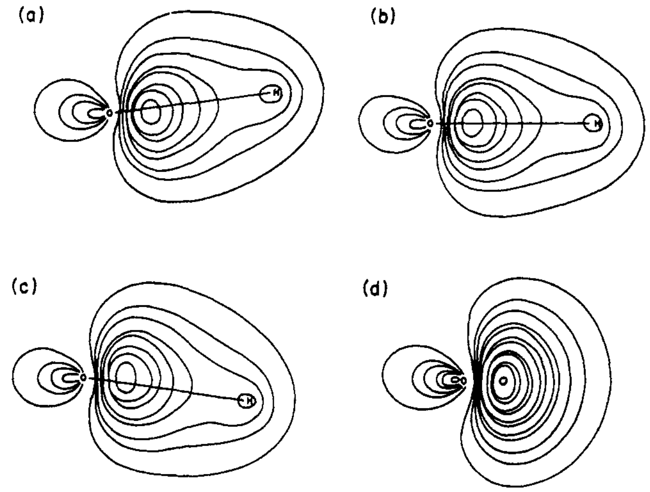

Figure 2. Contour diagrams of LMO densities in water: (a) bonding LMO at ∠HOH = 90.0°; (b) bonding LMO at ∠HOH = 104.52°; (c) bonding LMO at ∠HOH = 120.0°; (d) nonbonding LMO at ∠HOH = 104.52°. The same arbitrary coordinate system is used in the first three bonding LMO's. The outermost contour represents a density of 0.1; the density increases by 0.2 per contour as one works in toward the OH internuclear axis.

repulsion between the electron pairs is a minimum. When this idea is coupled with several simple postulates about interactions (*vide infra*), it becomes possible to rationalize and predict molecular geometries.[2]

In an attempt to compare the qualitative VSEPR theory with quantitative quantum chemistry we have considered a simple yet fundamental system which can be rigorously analyzed: the angular variation of the H_2O molecule as described by the LCAO–SCF–MO model. While the MO model is itself an approximate theory, it is rigorously defined, and as it gives a good prediction of the molecular geometry (see below) it is therefore acceptable. The approach taken was to transform the usual canonical (delocalized) MO's into a set of chemically appealing localized molecular orbitals (LMO) and then to examine directly either individual LMO interactions or various meaningful combinations of these. The LMO's were obtained by minimizing the total exchange energy between different orbitals.[3] This is just one of a number of possible localization criteria, but it does attempt to make the problem as "classical" as possible and has previously been widely employed for numerous other interpretative purposes.

Four levels of orbital expansions, all derived from atomic studies, were used: set I was a minimum basis set; set II was a double ζ quality or "split" basis set; set III was a "split" basis set including five additional 3-d type orbitals centered on the oxygen; and set IV was a "split" basis set with five atomic 3-d type orbitals centered on the oxygen and three 2-p type orbitals centered on each hydrogen.[4] It was found necessary to include an oxygen 3-d type orbital in the basis set to obtain reasonable agreement with the experimental HOH angle of 104.523°.[5] All orbital interactions were scaled by the procedure of McLean[7] to obtain both optimization of wave function and energy and satisfaction of the virial theorem. As is commonly the case, such scalings have trivial effects on the geometry. For nearly all calculations considered, the individual orbital interactions were found to be in qualitative agreement, and for the sake of brevity, only detailed data from set III will be presented, since it can be considered representative. Any deviation due to a difference in basis set will be noted as appropriate.

The simple VSEPR model of water places four essentially tetrahedrally directed electron pairs about the central oxygen atom (two O long pairs and O–H bond pairs). A schematic representation of such a system of orbitals is shown in Figure 1. Here each electron pair is treated as a hard object, *i.e.*, unable to penetrate into neighboring quadrants. Actually, there cannot be total localization among members of a set of delocalized orthonormal orbitals. Because of the "delocalized" nature of the wave functions and the stipulation of orthogonality, each localized hybrid has a negative back lobe in a neighboring hemisphere to ensure the cancellation of the overlap density with other orbitals. Figure 2 illustrates this nodal structure by showing orbital density contour diagrams for the bonding orbitals in three nuclear configurations as well as the lone pair orbital in the equilibrium configuration.

From the usual MO viewpoint most of the alteration in orbital interaction with angle variation can be generally explained by a general shift of electron density by both bonding and nonbonding orbitals toward the oxygen with increasing HOH angles. In contrast, the inner shell tends to transfer its density outwards. This is understood within the framework of the usual delocalized MO's by the observation that the $3a_1$ orbital, which acts as a bonding orbital in the bent configuration, becomes a π type, nonbonding orbital in the linear geometry. This overall electron migration with HOH angle is evident in Figure 2, as is also the rather interesting feature of orbital directionality. The O–H LMO's are somewhat "bent" for the nonequilibrium configurations of H_2O and generally tend to point in the direction of the equilibrium O–H bond. Thus, when the HOH angle is away from equilibrium, the O–H bond orbitals may be interpreted as tending to "pull" the angle back toward equilibrium. This is not too surprising, since the orthogonality requirements tend to force near tetrahedral orientation about oxygen. These results are in qualitative agreement with the work

(3) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).

(4) (a) M. E. Schwartz, *Chem. Phys. Lett.*, **6**, 631 (1970); (b) S. Huzinaga, *J. Chem. Phys.*, 42, 1293 (1965); (c) J. L. Whitten, *ibid.*, **44**, 359 (1966).

(5) The d orbital exponents were 0.718184, based on variational calculations at the equilibrium angle.[6]

(6) The uncertainty within each energetic sum was approximately 0.0001 hartree.

(7) A. D. McLean, *J. Chem. Phys.*, 40, 2774 (1964).

Table I. Individual Interaction Components as a Function of HOH Angle (degrees) for Basis Set III[a]

	90.0	100.0	104.52	110.0	120.0
T_{I}	30.73726	30.73352	30.73006	30.72512	30.71328
T_{B}	1.65392	1.64990	1.64870	1.64725	1.64567
T_{N}	1.98338	1.99092	1.99408	1.99787	2.00414
V_{IO}	−62.36430	−62.36344	−62.36161	−62.35844	−62.35003
V_{BO}	−7.26141	−7.27951	−7.28907	−7.30176	−7.32852
V_{NO}	−8.42817	−8.42291	−8.41952	−8.41457	−8.40305
V_{IH}	−0.55245	−0.55261	−0.55267	−0.55274	−0.55287
V_{BH}	−0.97722	−0.97757	−0.97637	−0.97384	−0.96615
$V_{\mathrm{BH'}}$	−0.45524	−0.43969	−0.43369	−0.42721	−0.41752
V_{NH}	−0.45821	−0.45949	−0.46027	−0.46137	−0.46385
J_{II}	4.84987	4.84963	4.84942	4.84906	4.84817
J_{IB}	0.89772	0.89987	0.90100	0.90251	0.90570
J_{IN}	1.03820	1.03765	1.03728	1.03673	1.03542
J_{BB}	0.82881	0.83294	0.83422	0.83536	0.83624
$J_{\mathrm{BB'}}$	0.57783	0.57257	0.57060	0.56856	0.56601
J_{BN}	0.61312	0.61364	0.61402	0.61462	0.61604
J_{NN}	0.87517	0.87256	0.87114	0.86919	0.86500
$J_{\mathrm{NN'}}$	0.65899	0.66193	0.66312	0.66449	0.66672
K_{IB}	0.01531	0.01530	0.01535	0.01537	0.01544
K_{IN}	0.02033	0.02050	0.02054	0.02063	0.02078
$K_{\mathrm{BB'}}$	0.03551	0.03453	0.03436	0.03436	0.03492
K_{BN}	0.04548	0.04522	0.04519	0.04525	0.04560
$K_{\mathrm{NN'}}$	0.05548	0.05706	0.05770	0.05841	0.05952
V_{nn}	9.23084	9.20245	9.19181	9.18037	9.16307
E_{total}	−76.02371	−76.03031	−76.03122	−76.03071	−76.02581

[a] Here and in the other tables the energy units are hartree atomic units (au): 1 hartree = 27.21 eV = 627.5 kcal/mol.

of Klessinger[8] who studied various geometries of H_2O using the SCGF model. In the special case of set I, one is able very simply to examine the direction of density as it originates from the oxygen, since the basis set is composed of a set containing a single set of 2-p type orbitals, which may be treated as orthogonal vectors. For the bonding hybrids, the angle between these p orbital density vectors goes from 101.7° for the ∠HOH = 90.0° to 96.4° for ∠HOH = 120.0°. There remains some ambiguity in correlating the p orbital density vectors with the total energetics of the system, since, *e.g.*, the optimum angle obtained by use of this minimum basis set expansion (set I) is approximately 110.0°, while the angle at which both internuclear angle and the p orbital density vectors coincide is ∼100.0°.

An alternate way of examining the orbital density directionality is by examining the angle between bonding orbital moments, which are well defined expectation values of the electronic position operators. Here each basis set was applicable to analysis. In general, this angle also lagged behind any variation from equilibrium by the HOH angle. For set III this angle ranged from 94.1° for ∠HOH = 90.0° to 108.9° for ∠HOH = 120.0°. At equilibrium it was slightly inside the OH line at 101.6°.

Before going into a direct analysis of energetics we shall establish some nomenclature. The total wave function ψ_t is expressed as the antisymmetric product of five doubly occupied localized orbitals: the inner shell, the two O–H bonding, and the two lone pair nonbonding orbitals

$$\Psi_t = A[\chi_{\mathrm{I}}{}^2\chi_{\mathrm{B}}{}^2\chi_{\mathrm{B'}}{}^2\chi_{\mathrm{N}}{}^2\chi_{\mathrm{N'}}{}^2]$$

where the subscripts I, B (and B′), and N (and N′) denote inner shell, bonding, and nonbonding, respectively. The interaction between these orbitals will be represented by the following symbols (atomic units used throughout).

$$J_{ij} = \left\langle \chi_i(1)\chi_i(1)\left|\frac{1}{r_{12}}\right|\chi_j(2)\chi_j(2)\right\rangle$$

coulomb interaction between orbitals χ_i and χ_j

$$K_{ij} = \left\langle \chi_i(1)\chi_j(1)\left|\frac{1}{r_{12}}\right|\chi_i(2)\chi_j(2)\right\rangle$$

exchange interaction between orbitals χ_i and χ_j

$$T_i = -{}^1/_2\langle\chi_i(1)|\nabla_1{}^2|\chi_i(1)\rangle$$

kinetic energy of orbital χ_i

$$V_{in} = -\left\langle \chi_i(1)\left|\frac{Z_n}{r_{1n}}\right|\chi_i(1)\right\rangle$$

nuclear potential between orbital χ_i and nucleus n

$$V_{nn} = \sum_{m<m'} Z_m Z_{m'}/R_{mm'}$$

total nuclear repulsion

Because the LMO's are obtained by a unitary transformation on the usual canonical SCF orbitals, they are, of course, equivalent overall to other representations. The total energy, which is invariant to any such unitary transformation, can be partitioned in terms of an orbital set as

$$E_{\mathrm{total}} = V_{nn} + 2\sum_i T_i + 2\sum_{i,n} V_{in} + \sum_{i,j}(2J_{ij} - K_{ij})$$

where the indices i and j run over the five doubly occupied LMO's and the index n runs over the three nuclei. Hereafter we assume interactions for LMO's only. Hopefully, there exist some subsets of the total energy expression which will be physically appealing and useful. We shall first consider the total electron-electron (repulsive) interaction energy (EI) with reference to VSEPR and later examine some alternate partitions.

The total energy of the water molecule, decomposed into its elementary interaction components, is shown in Table I for five nuclear configurations around the equilibrium angle. Examination of this table provides

---

(8) M. Klessinger, *Chem. Phys. Lett.*, 4, 144 (1969).

Table II. Summary of Distances between LMO Bond Moments

Angle, deg	D(B–B)[a]	D(N–N)	D(B–N)	D total[b]
		Basis Set I		
90.0	1.5000	1.0399	1.3341	7.8764
100.0	1.5544	1.0226	1.3302	7.8981[c]
104.52	1.5755	1.0144	1.3262	7.8945
110.0	1.5978	1.0040	1.3194	7.8793
120.0	1.6291	0.9835	1.3021	7.8211
		Basis Set III		
90.0	1.4449	1.0329	1.2964	7.6635
100.0	1.5023	1.0158	1.2962	7.7027[c]
104.52	1.5246	1.0074	1.2899	7.6918
110.0	1.5487	0.9964	1.2844	7.6825
120.0	1.5818	0.9766	1.2684	7.6319
		Basis Set IV		
90.0	1.4345	1.0252	1.2853	7.6008
104.52	1.5146	1.0014	1.2802	7.6369[c]
120.0	1.5701	0.9701	1.2603	7.5813

[a] Distance between the average electronic positions of two localized orbitals. [b] Sum of distances between all valence LMO bond moments. [c] Extrema.

Table III. Electronic Interaction Energy Excluding Inner Shell

Angle, deg	D[a]	IPVCR	IPVER	IPVR	EIV
			Basis Set I		
90.0	3.45283	14.79807	0.54239	14.25568	17.70851
100.0	3.45533[b]	14.81245	0.54396	14.26849	17.72382
104.52	3.45521	14.82445	0.54596	14.27849	17.73370
110.0	3.45409	14.84348	0.54934	14.29414	17.74824
115.0	3.45216	14.86517	0.55336	14.31181	17.76397
120.0	3.44934	14.89080	0.55824	14.33256	17.78190
			Basis Set III		
90.0	3.40795	14.75718	0.54582	14.21136	17.61932
100.0	3.41098[b]	14.75619[b]	0.54489[b]	14.21130[b]	17.62228
104.52	3.41072	14.75926	0.54566	14.21360	17.62432
110.0	3.40911	14.76608	0.54754	14.21854	17.62764
120.0	3.40249	14.78751	0.55366	14.23385	17.63635
			Basis Set IV		
90.0	3.40945	14.78904	0.55290	14.23614	17.64559
104.52	3.41293[b]	14.78792[b]	0.55206[b]	14.23586[b]	17.64880
120.0	3.40528	14.81609	0.56001	14.25608	17.66136

[a] Definitions of all abbreviations are found in text. [b] Extrema.

some interesting comparisons with the assumptions of VSEPR theory. One of the postulates[1] of the theory is that orbital electronic repulsive interactions vary according to

nonbonding–nonbonding > nonbonding–bonding > bonding–bonding

This point is consistent with both the calculated coulomb interactions between neighboring orbitals ($J_{\mathrm{NN'}} > J_{\mathrm{NB}} > J_{\mathrm{BB'}}$), and the total interaction between valence orbitals [$(4J_{\mathrm{NN'}} - 2K_{\mathrm{NN'}}) > (4J_{\mathrm{NB}} - 2K_{\mathrm{NB}}) > (4J_{\mathrm{BB'}} - 2K_{\mathrm{BB'}})$]. Another postulate of the VSEPR theory which is also consistent with these calculations is that valence orbitals are aligned so that a maximum distance between orbital centers is achieved. As shown in Table II, the calculated composite sum of distances between the LMO bond moments (*i.e.*, average position of electron in an orbital) is a maximum near an angle of 100.0°, thus suggesting an approximate coincidence between the equilibrium angle and the total interorbital average distances.

The total electronic interaction energy (EI) is

$$\mathrm{EI} = \sum_i J_{ii} + 4\sum_{i<j} J_{ij} - 2\sum_{i<j} K_{ij} \equiv \mathrm{D} + \mathrm{IPCR} + \mathrm{IPEI}$$

Here we have partitioned the total electronic energy into diagonal coulomb (D), interpair coulombic repulsion (IPCR), and interpair exchange interaction (IPEI), respectively. EI as a whole is invariant to any unitary transformation, and in the specific case of the localization procedure used here the transformation simultaneously minimizes the exchange and coulomb interactions between neighboring orbitals while it maximizes the diagonal interaction component.[3] EI was found to increase monotonically with increasing HOH angle over the region of interest (90–120.0°), at variance with VSEPR. It was found at all levels of basis set expansion that the exchange energy between the bonding and nonbonding orbitals experienced a shallow minimum in the neighborhood of the equilibrium angle. In addition, for the improved sets (III and IV) the exchange between adjacent bonding orbitals as well as the total exchange energy (IPEI) of the system passed through a minimum in the region of the equilibrium angle. This effect may be correlated to the observed *maximum* obtained for the *diagonal* coulomb components (D) of EI near the equilibrium configuration. The *total* off-diagonal coulombic interaction, though, did not show the anticipated complementary minimum. Alternatively, if only the valence orbital contributions to the electronic interaction energy (VEI) are considered, one finds that the diagonal (DV), the interpair valence exchange interaction (IPVEI), as well as the interpair valence coulombic repulsion (IPVCR) contributions show corresponding extrema in the vicinity of the equilibrium angle for the improved basis sets. Table III summarizes the valence electronic interaction energy (VEI), as well as its principal components for the basis sets considered here. The total interpair valence repulsion (IPVR), which is simply the sum of IPVEI and IPVCR, also passes through a minimum in the vicinity of the equilibrium angle when the improved basis expansions are considered. These results are in agreement with geminal calculations per-

Table IV. Summary of Variation in the Components of the Electronic Interaction Energy for Various Basis Set Expansions

Basis set	D[a]	IPCR	IPEI	EI	DV	IPVCR	IPVEI	VEI
I	+[b]	+	+	+	Max 100°	+	+	+
III	Max[c] 100°	+	Min 100°	+	Max 100°	Min 100°	Min 100°	+
IV	Max 105°	+	+	+	Max 105°	Min 105°	Min 105°	+

[a] Definition of energetic abbreviations found in context of text. [b] + denotes a monotonic energetic increase over angular range (90 → 120°). [c] All potential surfaces have relative variations of the same order of magnitude as the variation of the total energy (~5.0 kcal) over the same angular domain.

Table V. Valence Electron Repulsion Combinations Which Exhibit a Minimum Near the Equilibrium Geometry[a]

Combination	J_{BB}	$J_{BB'}$	$K_{BB'}$	J_{NN}	$J_{NN'}$	$K_{NN'}$	J_{BN}	K_{BN}	V_{nn}
1[b]	0	0	0	0	4	2	8	0	1
2[b]	0	0	0	2	4	2	16	0	1
3[b]	0	0	0	2	4	2	16	8	1
4[c]	0	4	0	0	0	0	16	0	0
5[c]	0	4	0	0	0	0	16	8	0
6[c]	0	4	2	0	0	0	16	0	0
7[c]	0	4	2	0	0	0	16	8	0
8[d]	2	0	0	0	0	0	16	0	1
9[b]	2	0	0	2	4	0	16	0	1

[a] Both extended basis sets III and IV pass through minima at equilibrium configuration. [b] Set I does not pass through a minimum in the immediate vicinity. [c] Set I passes through minimum at 100.0°. [d] Set I passes through minimum at 104.52°.

formed by Stevens[9] on H_2O using a double ζ quality basis set. Table IV summarizes all these electronic interaction components presented for the aid of the reader's analysis.

Turning to other analyses of the molecular energy, a potentially very simple scheme would be to find a quantity dependent formally only on individual LMO's. Takahata and Parr[10] emphasized that the only additive resolution of the total energy into individual orbital components is the kinetic energy

$$E_{\text{total}} = -2{\sum_i}' T_i$$

where the summation is over a particular set of doubly occupied molecular orbitals. Here it is assumed that the virial theorem holds, and we have scaled all our results (both total and component energies) to ensure this.[5,10] Takahata and Parr found by constructing a set of approximately localized equivalent orbitals from a minimum basis set MO wave function that changes in the lone pair orbital kinetic energy essentially regulate the equilibrium angle in H_2O. In contrast, we found no such correlation. Only in the case of set I did we find any coincidence between any individual orbital kinetic energy sum and the total energy of the system; here the kinetic energy of the bonding orbitals passed through a minimum at approximately 115.0°. But this effect completely disappeared for improved basis sets (II, III, and IV), and we were unable to establish any correlation of the total energetics of our system with any individual LMO kinetic energy component. The previously found effect[10] was due either to the sensitive nature of the definition of localized orbitals or to the quality of the basis set used in the MO expansions.

Another alternative to consideration of only EI and VSEPR would be to develop a simple "minimal model" where other simple combinations of the energy components are examined. For such energetic partitions to be useful they should give results which are not sensitive to basis set expansion; they should experience a pronounced minimum an order of magnitude greater than the uncertainty intrinsic to any single energetic component,[6] and, of course, they should correlate with simple chemical ideas.

A simple computer program was written to attempt to separate out such partitions which exhibited either a maximum or a minimum near the equilibrium configuration. Because of the large number of possible combinations of interactions, it was soon realized that additional constraints would have to be placed on these subsets. We chose the restriction that only those combinations of interactions which appeared to have built into them some semblance of chemical meaning would be considered. This was primarily accomplished by checking for consistency within orbital interactions. For example, if one bond pair enters an expression in a certain way, the other equivalent bond pair must enter in the same way. For a further discussion of this screening procedure, see ref 11. Even with this stringent requirement, hundreds of such interaction sums were determined for this problem, and we shall not discuss them here. Table V summarizes explicitly all such subsets which involve only coulombic and exchange interactions among the valence electrons, since such energetics are closely related to VSEPR. Even here there are nine combinations. Similarly Table VI summarizes those subsets which involve the bonding orbitals' interaction with their environment; *i.e.*, they do not explicitly contain the self-nonbonding interactions. Notice that most of these subsets involve V_{nn}. This appeared to be a general feature among a large majority of those subsets which exhibited extrema near

---

(9) W. S. Stevens, Thesis, Indiana University, 1971.

(10) Y. Takahata and R. G. Parr, *Chem. Phys. Lett.*, 4, 109 (1969).

(11) For a complete discussion see C. A. Naleway, Ph.D. thesis, University of Notre Dame, 1973.

Table VI. Bonding Orbital Interaction Combinations Which Exhibit a Minimum at the Equilibrium Geometry[a]

Combination	T_B	V_{HB}	$V_{HB'}$	J_{BB}	$J_{BB'}$	$K_{BB'}$	J_{NB}	K_{NB}	V_{nn}
1	0	0	0	2	0	0	16	0	1
2	0	4	0	2	0	0	0	0	1
3	2	2	2	0	4	0	8	0	1
4	2	2	2	0	4	0	8	4	1
5	4	4	0	0	0	0	16	0	1
6	4	4	0	0	0	0	16	8	1
7	4	4	0	0	4	0	8	0	0
8	4	4	0	0	4	0	8	4	0
9	4	4	0	0	4	2	8	0	0
10	4	4	0	0	4	2	8	4	0
11	4	4	0	2	0	0	16	0	1
12	4	4	0	2	0	0	16	8	1
13	4	4	0	2	4	2	8	0	0

[a] Basis sets I, III, and IV all pass through a minimum at the equilibrium configuration.

Table VII. Summary of a Few Energy Portions Involving Orbital Energies[a]

	90.0°	100.0°	104.52°	100.0°	120.0°
$\sum_{i=1}^{\text{all}} \epsilon_i$	−23.72027	−23.70194	−23.69330	−23.68224	−23.66014
$\sum_{i=1}^{\text{all}} (\epsilon_i + h_i^{(0)})$	−85.25454	−85.23276	−85.22303	−85.21108	−85.18874
$\sum_{i=1}^{\text{valence}} \epsilon_i$	−3.51061	−3.49493	−3.48717	−3.47743	−3.45786
$\sum_{i=1}^{\text{valence}} (\epsilon_i + h_i^{(0)})$	−32.31295	−32.29063	−32.28000	−32.26746	−32.24411
$V_{nn} + \epsilon_{\text{core}} + \Sigma_i h_i^{(0)}$	−72.51310	−72.53538	−72.54405	−72.55328	−72.56795

[a] ϵ_i represents the eigenvalue of orbital χ_i, *i.e.*, $[T_i + \Sigma_j(2J_{ij} - K_{ij})]$. $h_i^{(0)}$ represents the one-electron interaction energy, *i.e.*, $[T_i + \Sigma_n V_{in}]$

equilibrium. It is our subjective judgment that few chemists would have picked most of these subsets "by hand" on the basis of "chemical intuition." Although many such energetic compositions may have chemical significance, we obviously cannot decide, in general, between such interaction sums and those which only accidentally have extrema, for the very particular case of H_2O. There are, however, other subsets which merit mentioning. First is the sum of the nuclear repulsion plus the *total* valency energy (*i.e.*, the total energy minus all inner shell interaction). This sum also exhibits a minimum near equilibrium, so that it appears meaningful to attempt to describe geometric detail within the framework of a valence only description. Conversely, the total *self* energy, defined by

$$2\sum_{i}^{\text{all}}\left[T_i + \frac{1}{2}J_{ii} + \sum_{n} V_{in}\right]$$

passed through a *maximum* at the equilibrium angle.

Other such models have been proposed. Walsh, in his classical papers,[12] was able to obtain the correct molecular shape for many different molecular species by use of diagrams which plotted "orbital energy" *vs.* bond angle. These diagrams were used to predict molecular geometry by occupying the valence MO's with electrons. The optimum bond angle then corresponded to the minimum energy calculated as the orbital energy sum. There remains, though, an uncertainty over the precise definition of Walsh's orbital energies. Many hypotheses have been proposed in attempts to correlate common theoretical quantities with these levels.[13–16] The simplest relationship possible is an equivalence between "orbital energy" and orbital eigenvalue. The question then becomes, "Why should the sum of valence eigenvalues parallel the total energy of the system?" Allen[16] has pointed out that one should expect this parallel if the additional energetic components which compose the difference between the total energy and the sum of valence eigenvalues, *i.e.*, $[V_{nn} + \epsilon_{\text{core}} + \Sigma h_i^{(0)}]$, are collectively independent of angle. Table VII illustrates for the case of water that this quantity exhibits an angular dependence, and that the sum of orbital energies does not give a minimum anywhere near the correct angle.

A second possible candidate for "orbital energy" is discussed by Coulson and Neilson.[13] By adding onto the eigenvalue of each orbital the one-electron interaction energy with its environment, a set of energies ("partitioned energies") is obtained. The sum of this set yields the total electronic energy of the system. However, this sum does not include the nuclear repulsion which is essential to the total energetics in order to obtain the proper molecular geometry. Again (Table III) this sum does not predict the bond angle.

Summary and Conclusions

The LMO calculations are qualitatively consistent with VSEPR for this system, and we may, therefore, conclude that the general physical ideas underlying

---

[12] A. D. Walsh, *J. Chem. Soc., London*, 2260, 2266, 2288, 2296, 2301 (1953).

[13] C. A. Coulson and A. H. Neilson, *Discuss. Faraday Soc.*, **35**, 71 (1963).

[14] R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **45**, 3682 (1966).

[15] D. Peters, *Trans. Faraday Soc.*, **62**, 1353 (1966).

[16] L. Allen, *Theor. Chim. Acta*, **24**, 117 (1972).

VSEPR are reproduced faithfully by the complicated all electron MO scheme. However, the simple kinetic energy results obtained earlier by Takahata and Parr[9] were not found in our more elaborate studies, nor were the Walsh diagram type arguments effective. Other LMO energy partitions, however, showed minima near equilibrium, but any generalizations from these must await confirmation from similar applications to other molecules.

Acknowledgments. This work has been supported in part by a grant from the Research Corporation. The work described herein constitutes a portion of the Ph.D. thesis research of C. A. N. at the University of Notre Dame.

Photochemical and Spectroscopic Applications of Approximate Molecular Orbital Theory. I. Averaged Field Approximate Open Shell Theory

Robert R. Birge[1]

Contribution from the Hall-Atwater Laboratories, Wesleyan University, Middletown, Connecticut 06457. *Received March 6, 1973*

Abstract: An approximate procedure for obtaining self-consistent field wave functions for the first excited singlet state of polyatomic molecules is investigated. This procedure utilizes an averaged field Fock operator serving to reduce the three coupled SCF equations required in a normal singlet state open shell variational calculation to a single SCF equation within a slightly deorthogonalized basis field. The formalism, which is termed "average field approximate open shell" (AFAOS) theory, is applied to the CNDO and INDO procedures yielding favorable results. AFAOS calculations on a variety of molecules are presented. For polyatomic molecules containing 26 or more valence electrons, the AFAOS method yields wave functions of comparable accuracy to the more rigorous parent open shell theory of Kroto and Santry.

During the past decade, a number of approximate methods have been developed for obtaining self-consistent field molecular orbitals for all valence electrons of polyatomic molecules.[2-10] Although these procedures provide only qualitative information regarding the orbital nature and the density characteristics of the optical electrons, this information has often proved quite useful in rationalizing observed photochemical and spectroscopic phenomena.[11-13] While wave functions for the first excited triplet states of molecules (with closed shell ground states) can be generated using readily available unrestricted open shell procedures,[3,4,6] the complications involved in generating wave functions for the first excited singlet state (see below) have precluded the general use of wave functions optimized to the excited state singlet electron configuration. Accordingly, most LCAO investigations of excited singlets have relied on either virtual orbital techniques[7,12] or on the use of wave functions for the first excited triplet state when the differing symmetry of the open shell orbitals suggested that the singlet and triplet states would possess similar electron distributions.[13] The virtual orbital technique has the distinct disadvantage of optimizing the wave function for the ground state electron configuration. On the other hand, the use of triplet wave functions as an approximation for singlet wave functions, while often defended for CNDO calculations on σ,π^* (or n,π^*) states, is a dubious approach since many orbital interactions which are neglected in the unrestricted open shell calculation are important for the corresponding excited state singlet calculation.

Conventional SCF singlet state open shell variational procedures normally require the construction of three coupled SCF equations each requiring a separate Fock operator (see section I). These procedures require an approximate threefold increase in computation time relative to closed shell calculations and a computer code capable of monitoring the symmetries of the molecular orbitals since the order of the eigenvectors is occasionally different within the three orbital coefficient matrices.[8] The usual end result is a program limited to calculations on small basis set molecules.

In this article we investigate an approximate variational procedure for obtaining wave functions for the first excited singlet state of polyatomic molecules which utilizes an averaged field Fock operator serving to reduce the

---

(1) Department of Chemistry, Harvard University, Cambridge, Mass. 02138.

(2) Of the numerous approximate methods available, the CNDO and INDO procedures developed by Pople and coworkers[3-5] appear the more versatile and reliable.

(3) (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129, S136 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

(4) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967).

(5) D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967).

(6) J. A. Pople and R. K. Nesbet, *ibid.*, **22**, 571 (1954).

(7) H. W. Kroto and D. P. Santry, *ibid.*, **47**, 792 (1967).

(8) H. W. Kroto and D. P. Santry, *ibid.*, **47**, 2736 (1967).

(9) R. N. Dixon, *Mol. Phys.*, **12**, 83 (1967).

(10) G. A. Segal, *J. Chem. Phys.*, **53**, 360 (1970).

(11) R. R. Birge and P. A. Leermakers, *J. Amer. Chem. Soc.*, **94**, 8105 (1972).

(12) J. M. Hollas, E. Gregorek, and L. Goodman, *J. Chem. Phys.*, **49**, 1745 (1968); W. D. Chandler and L. Goodman, *J. Mol. Spectrosc.*, **36**, 141 (1970); **37**, 33 (1971); K. Yamaguchi and T. Fueno, *Bull. Chem. Soc. Jap.*, **44**, 43 (1971).

(13) D. R. Williams, *J. Chem. Phys.*, **55**, 4578 (1971).