Localized Orbitals. I. σ Bonds

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This paper presents a method for the delineation of a set of truly localized orbitals and uses a nonunitary transformation to convert the localized orbitals into equivalent orbitals which are suitable for molecular quantum-mechanical calculations. The localized orbitals, which are suitable for describing polyatomic molecules including large nonplanar ones, are generated on the premise that the atomic orbitals used in the construction of two-center one- or two-electron bonds should be such that, when overlap is totally neglected, each atomic orbital has the same calculated value of angular momentum about its bond axis. The nonunitary transformation is derived from the modification in the form of the general orthonormality conditions upon a change from overlap metric 1 to a realistic overlap matrix Δ. This approach is applied to methane, ammonia, and water to calculate the equivalent orbitals. System energies and dipole moments are also calculated, and these and the equivalent orbitals are compared with the results of reported SCF calculations. The close values of the energies show that this approach may be used for realistic calculations. It also has an advantage over SCF techniques in that extension to extremely complicated molecular systems is possible. Further, the orbitals used herein are particularly useful for chemists since they are couched in terms of localized-bond characteristics alone.

INTRODUCTION

For many years ground-state wavefunctions have been characterized in terms of approximate solutions of the molecular Hartree–Fock equations.[1] These solutions, the molecular orbitals (MO's) of the system, an antisymmetrized product of which comprises the total electronic wavefunction, possess the property that they transform according to the irreducible representations of the point group to which the molecule belongs. As such, these orbitals are delocalized over the entire molecule and cannot be interpreted in a framework consistent with established chemical concepts. In order to overcome this difficulty, equivalent orbitals[2] (EO's) or localized molecular orbitals[3] (LMO's) which emphasize the localized behavior of the orbitals have been constructed from linear combinations of these molecular orbitals. Since the MO's and the derived EO's or LMO's are connected by a unitary transformation, both sets of orbitals predict identical values for all observables. Because of the utility of the localized molecular orbitals, considerable work[3] has been done to determine the unitary transformation between the MO's and the LMO's and to devise criteria suitable to define localization. The equivalent and localized molecular orbitals thus obtained are, however, not completely localized so it is still not possible to isolate each electron pair within

a complicated molecule so as to make it seem that each pair resides within a region defined only on one or two centers.

The purpose of the study undertaken here is to derive a picture of the molecular ground-state wavefunction from a model based on *completely* localized bonds so that the molecule may be inspected in a framework compatible with chemical intuition. A mathematical transformation is presented to convert the rather artificial localized orbitals into a set of equivalent orbitals which is appropriate for quantum-mechanical calculations. In other words, the intent of this study is to see whether or not insight into the complicated nature of molecular electronic structure might be obtained by dissecting the total electronic wavefunction into an overlay of more simplified representations.

The procedure developed here has the obvious advantage over SCF techniques in that computational complexities in these are negligible in comparison with SCF calculations so that large molecules, inaccessible to SCF procedures, may be treated with relative ease. The criterion for the validity of such a procedure depends upon the fact that when molecules are characterized by both methods using the same basis set, the energy penalty paid in adopting the constraints on the wavefunction, which result from the present technique, is small.

Even without any knowledge of the molecular energy itself (or the integrals which permit its evaluation), a great deal of chemical information may be obtained from the ground-state wavefunction alone. That is to say, the dipole moment, quadrupole coupling constant, Mössbauer chemical shift, etc., may be calculated without a knowledge of the molecular energy. It will be shown in future publications that the equivalent orbitals derived from completely localized orbitals do indeed predict reasonable values for numerous quantum-mechanical operators.

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[1] C. C. J. Roothaan, Rev. Mod. Phys. **21**, 69 (1951).
[2] J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1, 14 (1949); G. G. Hall and J. E. Lennard-Jones, *ibid.* **A202**, 155 (1950); J. E. Lennard-Jones and J. A. Pople, *ibid.* **A202**, 166 (1950); and subsequent papers in that series.
[3] C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. **35**, 457 (1963); R. M. Pitzer, J. Chem. Phys. **41**, 2216 (1964); C. Edmiston and K. Ruedenberg, in *Quantum Theory of Atoms, Molecules and the Solid State, A Tribute to John C. Slater*, P.-O. Löwdin, Ed. (Academic Press Inc., New York, 1966) and other papers by Edmiston and Ruedenberg.

This paper describes the method for constructing the equivalent orbitals for a system of sigma bonds and applies this method to the study of methane, ammonia, and water. The second paper in the series will cover the application of the method to pi bonding and the third will discuss the use of d orbitals in sigma and pi bonding in molecules based on second-row elements.

METHOD

The "localized representation" is defined in terms of a set of orbitals, henceforth called localized orbitals (LO's), having the important property that each will be specified as a linear combination of atomic functions defined on only one or two centers. In essence, the polyatomic molecule will be represented as a superposition of diatomic molecules, the form of which is then modified to take into account the presence of others.

The molecular orbitals determined for diatomic molecules have certain interesting properties. First, σ, π, etc., are good quantum numbers, i.e., the angular momentum of the charge distribution of each molecular orbital as measured about the bond axis is quantized. This means that we might expect that the atomic orbitals used in building the localized orbitals should be such that the resulting charge distribution yields integral values of the angular momentum about the bond axis. Second, for diatomic molecules it is found that, all other things being equal, atomic orbitals of lower angular momentum are utilized preferentially over those of higher values.

When a polyatomic wavefunction is to be synthesized in the localized representation, a sequence of diatomic molecular orbitals is defined within a unit metric (i.e., nonoverlapping basis functions) using the selection rules that would hold had the others not existed. An exception is that when more than one LO is to be defined on a single center, the various linear combinations of atomic orbitals on this center must be such that they are orthogonal.

In the following section, the technique for delineating the set of localized orbitals is developed. The next section then describes the transformation necessary to ensure orthonormality of the equivalent orbitals in the chosen basis of Slater orbitals.

Construction of the Localized Orbitals

Let us consider a molecule in which the orbital overlap is artificially eliminated with no concomitant charge transfer. Then one would see the charge distributions directed along each of the original bond axes.

This situation corresponds to the requirements that each of the atomic orbitals possess the same value of the angular momentum about the bond axis[4] as would be

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[4] It should be noted that the angular momentum about an axis, e.g., z, as measured by the quantum number m is quite different from the angular momentum about a point as measured by the atomic orbital quantum number l.

found for a diatomic molecule based on the pair of atoms involved in the bond. Further, as discussed previously,[5,6] the angular momentum can have only integral values. In other words, when a σ bond is to be created, only those orbitals having an angular momentum of zero may be used if the bond axis is the z axis. When the bond axis is not the z axis, the addition rules of the spherical harmonics generate the appropriate selection rules. Likewise, for π bonds, $|m|$ must be unity, etc. This is the mathematical formulation of orbital following. However, the actual procedure employed is quite general and deviations from orbital following will be discussed later.

Given a Cartesian coordinate system in which one of the nuclei, say A, is located at the origin and another nucleus, say B, is located by the coordinates (x, y, z), then the atomic orbitals that are to be used on center A in the construction of a σ-molecular orbital are ${}^0\phi^A(s)$, ${}^0\phi_\sigma{}^A(p)$, and ${}^0\phi_\sigma{}^A(d)$ where

$${}^0\phi_\sigma{}^A(p) = \cos\eta \, \sin\epsilon \, {}^0\phi^A(p_x) + \cos\eta \, \cos\epsilon \, {}^0\phi^A(p_y)$$
$$- \sin\eta \, {}^0\phi^A(p_z),$$

$${}^0\phi_\sigma{}^A(d) = (1 - \tfrac{3}{2}\cos^2\eta) \, {}^0\phi^A(d_{z^2}) - \tfrac{1}{2}\sqrt{3} \, \sin2\eta \, \sin\epsilon \, {}^0\phi^A(d_{xz})$$
$$- \tfrac{1}{2}\sqrt{3} \, \sin2\eta \, \cos\epsilon \, {}^0\phi^A(d_{yz}) + \tfrac{3}{2} \cos^2\eta \, \sin2\epsilon \, {}^0\phi^A(d_{xy})$$
$$- \tfrac{1}{2}\sqrt{3} \, \cos^2\eta \, \cos2\epsilon \, {}^0\phi^A(d_{x^2-y^2}). \tag{1}$$

The basis atomic orbitals ${}^0\phi^A(s)$, ${}^0\phi^A(p_x)$, etc., are such that each is defined on center A and has the general form $f_{l,m}(r_A) Y_l{}^m(\theta, \phi)$ where the l and m quantum numbers are appropriate to the orbital mentioned. The function $f_{l,m}(r_A)$ is *not known or needed*. However, each must be such that the orthogonality of all basis atomic orbitals is assured. For orbital following, the angles η and ϵ are given by

$$\eta = \arcsin[-z/(x^2+y^2+z^2)^{1/2}],$$
$$\epsilon = \arctan(y/x). \tag{2}$$

The localized orbital is then written

$${}^0\psi_i = {}^0\gamma_{is_A} \, {}^0\phi^A(s) + {}^0\gamma_{ip_A} \, {}^0\phi_\sigma{}^A(p) + {}^0\gamma_{id_A} \, {}^0\phi_\sigma{}^A(d)$$
$$+ \text{similar terms on nucleus B.} \tag{3}$$

In this manner all σ LO's of the system may be formed. It should be remembered that the ${}^0\gamma_{ij}$ values are constrained by the fact that each ψ_i is orthogonal to all others. If Γ_0 is the matrix of ${}^0\gamma_{ij}$ values, this requires that

$$\Gamma_0 \Gamma_0{}^T = 1. \tag{4}$$

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[5] J. H. Letcher and J. R. Van Wazer, J. Chem. Phys. **44**, 815 (1966); **45**, 2926 (1966).

[6] J. H. Letcher and J. R. Van Wazer, *Topics in Phosphorus Chemistry*, M. Grayson and E. J. Griffith, Eds. (Interscience Publishers, Inc., New York, 1967), Vol. 5, Chap. 2.

It turns out that this is not quite sufficient to uniquely determine all of the $^0\gamma_{ij}$ values. In fact, there will be one arbitrary parameter for each different bond. It is chosen here to be represented by the parameter h_i which is set equal to the sum of the squares of the $^0\gamma_{ij}$ values of common i defined on one nucleus. In the above example this would be

$$h_{i_A} = {}^0\gamma_{is_A}{}^2 + {}^0\gamma_{ip_A}{}^2 + {}^0\gamma_{id_A}{}^2 \qquad (5)$$

and would include all functions in ψ_i defined on nucleus A. Within this artificial representation, this parameter has a straightforward physical interpretation as the average amount of charge residing in the atomic orbitals of one nucleus in a two-center bond. This parameter shall be referred to as the *bond polarity coefficient*. Note that in the above discussion complete orbital following was assumed and it is fundamental to this method. If this assumption is not made, then one obtains an angular parameter (θ_{ij}) for each unique bond angle in the molecule unless symmetry considerations dictate this angle (as they do in methane).

From the preceding discussion it is seen that all σ LO's can be expressed in terms of only the bond angles (or angular parameters) and the defined bond polarity coefficients.

The Delta Transformation[7]

A set of LO's, EO's, MO's, or LMO's $\{\psi_i\}$ may be represented as a column vector $\boldsymbol{\psi}$ in which $(\boldsymbol{\psi})_i = \psi_i$. The orbitals are orthonormal, i.e.,

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \qquad (6)$$

or

$$\boldsymbol{\psi}\boldsymbol{\psi}^T = 1. \qquad (7)$$

In the LCAO approximation each function ψ_i is represented as a sum over atomic orbitals defined on each of the nuclei in the system. That is,

$$\psi_i = \sum_j \gamma_{ij}\phi_j \qquad (8)$$

or

$$\boldsymbol{\psi} = \boldsymbol{\Gamma}\boldsymbol{\phi}. \qquad (9)$$

The overlap matrix $\boldsymbol{\Delta}$ is defined by

$$(\boldsymbol{\Delta})_{ij} = \langle \phi_i | \phi_j \rangle \qquad (10)$$

or

$$\boldsymbol{\Delta} = \boldsymbol{\phi}\boldsymbol{\phi}^T. \qquad (11)$$

For the orbitals ψ_i to be orthogonal,

$$\boldsymbol{\Gamma}\boldsymbol{\Delta}\boldsymbol{\Gamma}^T = 1. \qquad (12)$$

We say then that the coefficients are orthonormal in the metric $\boldsymbol{\Delta}$.

The form of a matrix of coefficients $\boldsymbol{\Gamma}_0$ for any wavefunction expressed in terms of a set of basis functions $\boldsymbol{\phi}_0$ would also have the same form, i.e.,

$$\boldsymbol{\Gamma}_0\boldsymbol{\Delta}_0\boldsymbol{\Gamma}_0{}^T = 1, \qquad (13)$$

where

$$\boldsymbol{\phi}_0\boldsymbol{\phi}_0{}^T = \boldsymbol{\Delta}_0.$$

Since $\boldsymbol{\Delta}$ and $\boldsymbol{\Delta}_0$ are both real, positive definite, symmetric matrices, $\boldsymbol{\Delta}_0{}^{1/2}$ and $\boldsymbol{\Delta}^{-1/2}$ exist[8] and are symmetric. Therefore, $\boldsymbol{\Gamma}_0\boldsymbol{\Delta}_0\boldsymbol{\Gamma}_0{}^T$ can be rewritten

$$\boldsymbol{\Gamma}_0\boldsymbol{\Delta}_0\boldsymbol{\Gamma}_0{}^T = \boldsymbol{\Gamma}_0\boldsymbol{\Delta}_0{}^{1/2}\boldsymbol{\Delta}_0{}^{1/2}\boldsymbol{\Gamma}_0{}^T = \boldsymbol{\Gamma}_0\boldsymbol{\Delta}_0{}^{1/2}\boldsymbol{\Delta}^{-1/2}\boldsymbol{\Delta}\boldsymbol{\Delta}^{-1/2}\boldsymbol{\Delta}_0{}^{1/2}\boldsymbol{\Gamma}_0{}^T$$

$$= [\boldsymbol{\Gamma}_0\boldsymbol{\Delta}_0\boldsymbol{\Delta}^{-1/2}]\boldsymbol{\Delta}[\boldsymbol{\Gamma}_0\boldsymbol{\Delta}_0{}^{1/2}\boldsymbol{\Delta}^{-1/2}]^T. \qquad (14)$$

Because of the similarity of the terms in Eqs. (14) and (12), it seems reasonable to make the association

$$\boldsymbol{\Gamma} = \boldsymbol{\Gamma}_0\boldsymbol{\Delta}_0{}^{1/2}\boldsymbol{\Delta}^{-1/2}. \qquad (15)$$

Thus, by knowing a particular set of localized orbitals $\boldsymbol{\psi}_{LO} = \boldsymbol{\Gamma}_0\boldsymbol{\phi}_0$ expressed in terms of basis functions the form of which is not completely known, it is asserted that the legitimate equivalent orbitals for the molecule are $\boldsymbol{\psi} = \boldsymbol{\Gamma}\boldsymbol{\phi}$ where $\boldsymbol{\Gamma}$ is expressed by Eq. (15). The two sets of orbitals ($\boldsymbol{\psi}_{EO} \equiv \boldsymbol{\Gamma}\boldsymbol{\phi}$ and $\boldsymbol{\psi}_{LO} \equiv \boldsymbol{\Gamma}_0\boldsymbol{\phi}_0$) are expressed in two different vector spaces and Eq. (15) is assumed valid only by association of terms of similar form. Therefore, a unitary transformation between $\boldsymbol{\psi}_{EO}$ and $\boldsymbol{\psi}_{LO}$ does not exist. Whether or not Eq. (15) and the specification of $\boldsymbol{\Gamma}_0$ represent a meaningful procedure is tested in the following sections by comparison of SCF findings with the results of the application of this method for three electronically different molecules.

That this is indeed a *method* for defining sets of legitimate equivalent orbitals is seen in the fact that in any case, $\boldsymbol{\phi}$ may be readily defined (e.g., STO's), then $\boldsymbol{\Delta}$ may easily be calculated by established techniques. The matrix of localized orbital coefficients $\boldsymbol{\Gamma}_0$ may be determined in a straightforward manner from internuclear distances, bond angles, and from a set of bond polarity coefficients (one for each LO, symmetry notwithstanding). These input data may be defined *a priori* or adjusted to match experimental data so that these functions might be used in later calculations. The *validity* of this method is tested by noting the strong similarities that occur when results of reported SCF calculations on a sequence of dissimilar molecules are compared with the coefficients of the equivalent orbitals calculated by the method presented herein and the system energies and molecular dipole moments computed from these EO's. (In the calculation of the EO's the sets of basis orbitals $\boldsymbol{\phi}$ used are, of course, the same

[7] This transformation was originally derived for a different purpose by P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

[8] The square root (or inverse square root) of a positive definite, symmetric matrix can be easily obtained by diagonalizing the matrix, taking the square root (or inverse square root) of the diagonal elements, and then undiagonalizing, i.e., $\boldsymbol{\Delta}^m = \mathbf{U}[(\mathbf{U}^T\boldsymbol{\Delta}\mathbf{U})^m]\mathbf{U}^T$ where $\mathbf{U}$ is the matrix which diagonalized $\boldsymbol{\Delta}$ and, in this case, $m = \pm\frac{1}{2}$.

as those employed in the SCF work.) It is therefore assumed that if this technique works well for molecules as different electronically as methane, ammonia, and water, the method will work with the same accuracy when dealing with larger more complicated molecules inaccessible to SCF methods.

In summary, to convert from the localized representation ($\Delta_0 = 1$, where each ϕ_0 has the properties defined previously) to the equivalent orbital representation, Δ need be specified only for the atomic orbitals to be used in the equivalent orbital representation (i.e., Slater orbitals, hydrogenic orbitals, etc.,) and

$$\Gamma = \Gamma_0 \Delta^{-1/2}, \quad (16)$$

so that

$$\psi_{EO} = \Gamma\phi = \Gamma_0 \Delta^{-1/2}\phi. \quad (17)$$

Treatment of CH_4, NH_3, and H_2O

The results of LCAO MO SCF calculations on methane,[9] ammonia,[10] and water[11] have been reported. Also, the localized molecular orbitals of water[3] and ammonia[12] have been obtained by maximizing the intraorbital Coulomb and exchange interactions while the equivalent orbitals of methane have been calculated according to the prescription of Lennard-Jones.[2] Since this series of molecules has zero, one, and two unshared pairs, it offers a chance to study not only the effects of the delta transformation on the inner-core orbitals but also those orbitals which are completely defined on one center in the localized representation, i.e., lone-pair orbitals.

Tables I–III compare the LCAO MO SCF equivalent and/or localized molecular orbitals with those obtained from the delta transformation, using various criteria to fix the parameters in the localized orbitals. The last calculation (d) employs a bond polarity coefficient estimated from Pauling electronegativities[13] and the Hannay–Smyth[14] formula for ionicity of bonds,

$$h_B = 1.0 + 0.16(\chi_A - \chi_B) + 0.035(\chi_A - \chi_B)^2, \quad (18)$$

and the angular parameter was set equal to the geometrical bond angle. In the next calculation (c) the angular parameter remained fixed at the bond angle and the bond polarity coefficient was varied to minimize the energy. In the last calculation (b) all parameters were varied to minimize the energy. It should be noted that the EO's obtained from the LO's by the delta transformation are not identical to the EO's obtained from the LCAO MO SCF MO's even when completely

[9] R. M. Pitzer, J. Chem. Phys. **46**, 4871 (1967).
[10] W. E. Palke and W. N. Lipscomb, J. Am. Chem. Soc. **88**, 2384 (1966).
[11] D. Merrifield (unpublished results).
[12] U. Kaldor, J. Chem. Phys. **46**, 1981 (1967).
[13] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, N.Y., 1960).
[14] N. B. Hannay and C. P. Smyth, J. Am. Chem. Soc. **68**, 171 (1946).

TABLE I. A comparison of the localized molecular orbitals (a) with the equivalent orbitals for methane obtained by (b) minimizing the energy with respect to h_H and (c) choosing h_H from the Hannay–Smyth formula. (θ is chosen to be tetrahedral for symmetry reasons)

Run	Parameters θ	h_H	Energy	Type[b]	H_1	H_2	H_3	H_4	1sC	2sC	$2p_zC$	$2p_zC$	$2p_zC$	$2p_yC$
(a)	LCAO MO SCF[a]		-40.0444	i.s.	-0.0060	-0.0060	-0.0060	-0.0060	0.9951	0.0300	0.0	0.0	0.0	0.0
				CH_1	0.5220	-0.0883	-0.0883	-0.0883	-0.1042	0.3499	0.2944	0.2944	0.2944	0.2944
(b)	109.5°	1.1106	-39.9782	i.s.	0.0184	0.0184	0.0184	0.0184	1.0227	-0.1606	0.0	0.0	0.0	0.0
				CH_1	0.5116	-0.1128	-0.1128	-0.1128	-0.0476	0.4018	0.2887	0.2887	0.2887	0.2887
(c)	109.5°	1.0696	-39.9733	i.s.	0.0184	0.0184	0.0184	0.0184	1.0227	-0.1606	0.0	0.0	0.0	0.0
				CH_1	0.5409	-0.1130	-0.1130	-0.1130	-0.0462	0.3833	0.2764	0.2764	0.2764	0.2764

[a] The localized molecular orbitals in this case were obtained by the criterion of J. E. Lennard-Jones, Proc. Roy. Soc. (London) A198, 14 (1949).

[b] In this table and the ones to follow i.s. is inner-shell orbital, XH_1 is X–H, bonding orbital, l.p. is lone-pair orbital.

TABLE II. A comparison of the localized molecular orbitals (a) of ammonia with the equivalent orbitals generated (b) by minimizing the energy with respect to both θ and h_H, (c) by setting $\theta=106°$ and minimizing the energy with respect to h_H, and (d) by setting $\theta=106°$ and determining h_H from Pauling electronegativities and the Hannay–Smyth formula.

| | Parameters | | | | | Wavefunction | | | | | | |
Run	θ	h_H	Energy	Dipole moment	Type	H_1	H_2	H_3	$1sN$	$2sN$	$2p_xN$	$2p_zN$
(a)	LCAO MO	SCF	−56.0052	1.76 D	i.s.	−0.0150	−0.0150	−0.0150	1.0162	−0.0867	0.0344	0.0
					l.p.	−0.0659	−0.0659	−0.0659	−0.0606	0.6714	−0.7914	0.0
					NH_1	0.5168	−0.0979	−0.0979	−0.0462	0.3141	0.2509	0.4829
(b)	104°	1.1229	−55.9233	1.81	i.s.	0.0200	0.0200	0.0200	1.0233	−0.1487	−0.0098	0.0
					l.p.	−0.1300	−0.1300	−0.1300	−0.0884	0.8169	−0.7136	0.0
					NH_1	0.5097	−0.0839	−0.0839	−0.0387	0.2890	0.2632	0.4976
(c)	106°	1.1292	−55.9215	1.91	i.s.	0.0200	0.0200	0.0200	1.0233	−0.1487	−0.0098	0.0
					l.p.	−0.1090	−0.1090	−0.1090	−0.0803	0.7387	−0.7625	0.0
					NH_1	0.5024	−0.0873	−0.0873	−0.0413	0.3133	0.2434	0.5003
(d)	106°	1.1724	−55.9167	2.12	i.s.	0.0200	0.0200	0.0200	1.0233	−0.1487	−0.0098	0.0
					l.p.	−0.1090	−0.1090	−0.1090	−0.0803	0.7387	−0.7625	0.0
					NH_1	0.4752	−0.0871	−0.0871	−0.0426	0.3287	0.2510	0.5188

TABLE III. A comparison of the localized molecular orbitals (a) of water with the equivalent orbitals derived (b) by minimizing with respect to θ and h_H, and (d) by setting $\theta=105°$ and minimizing with respect to h_H, and (d) by setting $\theta=105°$ and calculating h_H from the Hannay–Smyth formula.

| | Parameters | | | | | Wavefunction | | | | | | |
Run	θ	h_H	Energy	Dipole moment	Type	H_1	H_2	$1sO$	$2sO$	$2p_xO$	$2p_zO$	$2p_yO$
(a)	LCAO MO	SCF[a]	−75.6556	1.43 D	i.s.	0.0039	0.0039	−0.9922	0.1202	−0.0348	0.0	0.0
					l.p.	−0.1019	−0.1019	0.0946	0.6531	−0.3758	0.0	−0.7070
					OH_1	0.5659	−0.1609	0.0139	0.2260	0.4132	0.4122	0.0
(b)	98°	1.1188	−75.6102	1.10	i.s.	0.0180	0.0180	1.0233	−0.1401	−0.0078	0.0	0.0
					l.p.	−0.1374	−0.1374	−0.0834	0.7388	−0.3041	0.0	−0.7071
					OH_1	0.5672	−0.1280	−0.0279	0.1793	0.4236	0.4291	0.0
(c)	105°	1.1569	−75.5863	1.82	i.s.	0.0180	0.0180	1.0233	−0.1401	−0.0078	0.0	0.0
					l.p.	−0.1039	−0.1039	−0.0725	0.6382	−0.4191	0.0	−0.7071
					OH_1	0.5272	−0.1419	−0.0396	0.2845	0.3850	0.4431	0.0
(d)	105°	1.2798	−75.5628	2.44	i.s.	0.0180	0.0180	1.0233	−0.1401	−0.0078	0.0	0.0
					l.p.	−0.1039	−0.1039	−0.0725	0.6382	−0.4191	0.0	−0.7071
					OH_1	0.4534	−0.1345	−0.0431	0.3226	0.4142	0.4844	0.0

[a] Orthogonalized ($1s$) and ($2s$) orbitals have been used.

optimized and hence do not predict identical expectation values.

All calculations employed minimum basis sets with orbital exponents chosen by Slater's rules[15] except for ammonia for which the hydrogen exponent was 1.2. For a further discussion of basis sets and geometry, the reader is referred to the original LCAO–MO–SCF calculations.

DISCUSSION AND CONCLUSIONS

We note from the tables that in the case of water and ammonia that the bond polarity coefficient h_H is lower than that predicted with the use of Pauling electronegativities and the Hannay–Smyth formula. In methane just the opposite is true. In line with recent work on electronegativities[16] and ionic characters of bonds,[15] this result also suggests modifications on the Hannay–Smyth formula and/or the electronegativities because of hybridization effects. One might argue that the observed results could be due to inadequate basis sets; however, calculations were also carried out on water with an optimized minimum basis set[15] and essentially identical conclusions can be drawn.

Looking for trends we note that for the completely optimized set the angular parameter approaches the geometrical bond angle as the number of lone pairs decrease. The optimized angles[17] of 98° for water and 104° for ammonia are close to the angles found from the localized molecular orbitals although the angles cannot be strictly compared since the above angular parameters refer to the wavefunction *before* the transformation.

In reference to the completely optimized wavefunctions (b), the reader should note that the inner shell is fixed by the delta transformation and cannot be varied. An examination of the coefficients of the bonding and lone-pair orbitals reveals that the orbitals are better represented by the geometrically constrained orbitals (c) than the completely optimized ones (b). In ammonia, for instance, the sum of the squares of the deviations of the equivalent bonding and lone-pair orbitals from the localized molecular orbitals is 0.0121 for the geometrically constrained orbitals and 0.0418 for the completely optimized orbitals. This probably results from a biasing of the parameters (h_B, θ_{AB}) by the

rigidity of the inner shell. Such a result cautions against the use of indiscriminate optimization.

In all cases the dipole moment as well as the energy was improved by decreasing the amount of charge transfer (indicated by $1-h_B$). Thus, minimizing with respect to h_A *while geometrically constraining* θ appears to be a valid and useful procedure. Further, this strongly advocates the use of an improved electronegativity scale, one which take into account hybridization, etc., and a new means of relating the ionic character of a bond to the electronegativity difference of its two constituent atoms. Note that this optimization improves the bonding orbital while not affecting the lone pair.

Work has been done to try to fit sets of experimentally observed quantities to parameters defining molecular orbitals in the hope that a consistent set of values could be found. Flygare and Weiss[18] used a technique for specifying their set ψ_{EO}' by the relationship (in the notation of this paper, with each matrix having the same meaning) $\psi_{EO}' = [\Gamma_0 \Delta \Gamma_0^T]^{-1/2} \Gamma_0 \phi$ whereas in the present work $\psi_{EO} = \Gamma_0 \Delta^{-1/2} \phi$ is suggested. The Γ_0 matrix used by Flygare and Weiss for the formaldehyde molecule is that which is calculated by the method of Letcher and Van Wazer[5,6] (with essentially the same LO parameters) and is consistent with the technique presented herein. However, Flygare and Weiss offer no suggestions concerning the way the Γ_0 matrices can be calculated for any other molecule (including nonplanar and/or larger ones). Indeed, their work indicates that the constraints offered by the method presented here have a negligible effect on the accuracy of certain calculations of various experimental observables. This is likewise substantiated by the work of Sovers, Karplus, and Kern.[19]

With the results and techniques presented here, calculations can be done with ease on large polyatomic molecules. This work shows that the orbitals so derived bear sufficient resemblance to the localized molecular orbitals obtained from an SCF calculation to justify such a use. The technique presented here can be used to: (a) determine the sensitivity of various properties to the exact form of the wavefunction and (b) study the various properties of a molecule in a semiempirical manner in hopes that reasonable results can be obtained by adjusting a few parameters all of which have reasonable values. Such work is in progress.

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