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Natural Hybrid Orbitals

J. P. Foster and F. Weinhold*

Contribution from the Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706. *Received December 13, 1979*

Abstract: From the information contained in the (exact or approximate) first-order density matrix, we describe a method for extracting a unique set of atomic hybrids and bond orbitals for a given molecule, thereby constructing its "Lewis structure" in an a priori manner. These *natural* hybrids are optimal in a certain sense, are efficiently computed, and seem to agree well with chemical intuition (as summarized, for example, in Bent's Rule) and with hybrids obtained by other procedures. Using simple INDO-SCF-MO wave functions, we give applications of the natural hybrid orbital analysis to molecules exhibiting a variety of bonding features, including lone pairs, multiple bonds, strained rings, and "bent bonds", multiple resonance structures, hydrogen bonds, and three-center bonds. Three examples are described in greater detail: (i) "orbital following" during ammonia umbrella inversion, (ii) the dimerization of water molecules, and (iii) the hydrogen-bridged bonds of diborane.

I. Introduction

Orbital hybridization is among the most useful valence concepts. As originally formulated by Pauling[1] and Slater,[2] the sp^n hybrids of a central atom depend only on the number of ligands to be bonded, but for inequivalent ligands or unequal bond angles it is necessary to consider more general sp^λ hybrids of the form

$$h_\lambda(\theta) = N(s + \lambda^{1/2}p_\theta)$$

where p_θ is a normalized p orbital pointing in the direction θ, N is a normalization constant, and λ is generally noninteger.[3] As a matter of conceptual economy it is desirable to know the "best" such hybrids for a given molecule, since the parameters λ and θ can be related to molecular geometry,[4] NMR spin-spin coupling constants,[5] acid-dissociation constants,[6] and other measurable properties of interest.[7] Recently, the construction of such hybrids has acquired additional importance in connection with the use of bond orbital basis sets for molecular calculations, particularly in the LCBO (linear-combination-of-bond-orbitals) formulation of SCF-MO theory.[8]

It has long been realized that an optimal choice of hybrids for a given central atom A must depend on the nature, as well as the number and orientation, of the attached ligands L. A particularly important relationship between the hybrid p character (λ) and the electronegativity difference of A and L is summarized in Bent's Rule,[9] which states that an atom tends to direct hybrids of greater p character toward more electronegative ligands. The original idea for the construction of hybrids was based on the maximization of orbital amplitude in the direction of the bond to be formed. Murrell[10] generalized this idea by requiring the hybrids to have maximum overlap with the ligand orbital to be bonded, thus taking account of the *type* of ligand as well as its direction. Golebiewski[11] and Lykos and co-workers[12] showed how Murrell-type hybrids could be conventionally obtained by direct matrix diagonalization rather than by iterative or numerical methods, and other extensions were subsequently considered such as the simultaneous treatment of central atom and ligand hybrids[13] and inclusion of bond polarity.[14] Del Re[15] introduced the related notion of "overlap localization", in which hybrids were chosen to transform the overlap matrix as nearly as possible to a set of 2 × 2 diagonal blocks. Modifications of Del Re's procedure were subsequently found necessary to improve the description of atoms with lone pairs.[16]

Although maximum-overlap hybrids have been obtained for a number of systems,[17] one might question this approach in terms of its uncertain theoretical basis, the need for empirical information (e.g., bond energies) as weighting factors, and a degree of arbitrariness in the treatment of lone pairs. As pointed out by Peters,[18] the overlap integral may be useful in determining the relative strengths of a set of similar bonds but lacks flexibility for dealing with general bonds. Coulson and co-workers[19] derived hybrids for cyclopropane from a more rigorous energy-minimization criterion and showed that these agreed well with conventional maximum-overlap hybrids. Bartlett and Öhrn[20] found that the overlap criterion leads to good wave functions for a number of other covalent systems, as judged by the calculated energies. Since hybrids based on a direct energy-minimization criterion require significantly greater computational effort, they have not been widely employed.

An intermediate scheme, having a close relationship to the method proposed here, was introduced by McWeeny and Del Re.[21] These workers sought to numerically transform the first-order density matrix to 2 × 2 block-diagonal form (as in Del Re's analogous transformation of the overlap matrix) while simultaneously minimizing the associated SCF energy. This method incorporated a more rigorous energetic criterion for the selection of hybrids but is considerably more laborious than modified Murrell-type schemes. A somewhat related method was developed by Newton et al.,[22] who transformed canonical SCF orbitals to "localized" (LMO) form by the Edmiston-Ruedenberg procedure[23] and then extracted the portion of each LMO belonging to the central atom as the appropriate hybrid. This method has been employed for a number of strained compounds,[24] but the preliminary formation of LMO's is itself a laborious computational task,

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and the resulting hybrids are generally nonorthogonal, making comparisons with more conventional hybrids of uncertain significance. More recently, Kirtman et al.[25] have investigated the idea of "pointwise" hybridization by expanding SCF electron densities at various spatial points in a multipole series. Each of these methods makes some reference to the results of SCF–MO calculations and thus indirectly incorporates some aspects of the energy-minimization criterion which is omitted in maximum-overlap procedures.

In this paper we wish to describe a somewhat different procedure for constructing directed orthonormal hybrid orbitals, which has proven to be effective in bond orbital studies. Although most closely related to the McWeeny–Del Re scheme,[21] our procedure requires no simultaneous minimization of the SCF energy expression and indeed makes no special reference to the SCF approximation. Rather, the hybrids are derived only from the first-order density matrix (approximate or exact) and thus can be calculated at any desired level of accuracy. Since the hybrids we describe share some of the optimal properties associated with natural spin orbitals,[26] we refer to them as *natural hybrid orbitals* (NHO's) (associated with "natural bond orbitals", "natural polarization parameters", and so forth). As will be seen, the NHO procedure is numerically efficient, requires no preconceptions regarding the number or type of chemical bonds, and applies readily to diverse bonding situations such as those involving bent bonds, strained rings, lone pairs, weak intermolecular complexes, and three-center "bridge" bonds. Where comparisons are possible, the NHO's seem to agree reasonably well with hybrids determined by other methods.

The method of constructing natural hybrids is described in the following section II. In section III we exhibit NHO's for a variety of molecules (calculated at the semiempirical INDO–SCF–MO approximation level), comparing these where possible with results of other procedures. We also give more detailed numerical results for three special examples: (i) the umbrella inversion of ammonia, (ii) the formation of the water dimer by hydrogen bonding, and (iii) three-center bonding in diborane. Section IV summarizes and offers concluding remarks.

II. Maximum-Occupancy Hybrids and Natural Hybrids

The distribution of electron density in a closed-shell system with wave function $\psi(1, 2, ..., N)$ is described by the spinless first-order reduced density operator $\gamma(1|1')$[26]

$$\gamma(1|1') = N\int \psi(1, 2, ..., N)\psi^*(1', 2, ..., N)\ \mathrm{d}2...\mathrm{d}N \qquad \text{(II.1)}$$

In terms of the matrix elements

$$P_{kl} = \int \chi_k^*(1)\gamma(1|1')\chi_l(1')\ \mathrm{d}1\ \mathrm{d}1' \qquad \text{(II.2a)}$$

the expansion of $\gamma(1|1')$ in a complete orthonormal basis set of atomic orbitals $\{\chi_k\}$ takes the form

$$\gamma(1|1') = \sum_{k,l} P_{kl}\chi_k(1)\chi_l^*(1') \qquad \text{(II.2b)}$$

The diagonal element P_{kk} of the density matrix $\mathbf{P} = \{P_{kl}\}$ measures the occupancy of orbital χ_k in the wave function ψ. Thus, when the χ_k's are orthonormal bond orbitals formed from a set of atomic hybrids, one can define those hybrids as "best" which lead to bond orbitals of maximum occupancy

$$\sum_{\text{bond orbitals } k} P_{kk} = \max \qquad \text{(II.3a)}$$

or, equivalently, to antibond orbitals of minimum occupancy

$$\sum_{\text{antibond orbitals } l} P_{ll} = \min \qquad \text{(II.3b)}$$

This was essentially the method employed by Brunck and Weinhold[8] to choose optimal values of bond polarization parameters, but it can obviously be adapted to the determination of hybridization parameters as well. We refer to the hybrids thus determined as "maximum-occupancy hybrids" to distinguish them from the "natural hybrids" to be discussed below. Such maximum-occupancy hybrids are indeed the best possible choice, in the sense that the associated approximate wave function of doubly-occupied bond orbitals will have the best possible overlap with the exact ψ. However, in practice these hybrids must be determined from the defining equation (II.3) by numerical search techniques, which become laborious as the molecular size increases. Thus, we seek an alternative approach which leads more directly to hybrids having, as nearly as possible, the desired properties (eq II.3).

The orbitals of maximum occupancy, the natural spin orbitals, can be computed directly as eigenvectors of the full density matrix $\mathbf{P}$. However, in seeking optimal hybrid orbitals for atom A, we are concerned with maximizing the occupancy of orbitals *on A* which are participating in a bond with atom L. Accordingly, we first partition $\mathbf{P}$ into atomic subblocks (see eq II.4) and consider

$$\mathbf{P} = \begin{bmatrix} \mathbf{P}_{\mathrm{AA}} & \mathbf{P}_{\mathrm{AB}} \cdots \mathbf{P}_{\mathrm{AL}} \cdots \\ \mathbf{P}_{\mathrm{BA}} & \mathbf{P}_{\mathrm{BB}} \cdots \mathbf{P}_{\mathrm{BL}} \cdots \\ \vdots & \vdots \\ \mathbf{P}_{\mathrm{LA}} & \mathbf{P}_{\mathrm{LB}} \cdots \mathbf{P}_{\mathrm{LL}} \cdots \\ \vdots & \vdots \end{bmatrix} \qquad \text{(II.4)}$$

now the submatrix $\mathbf{P}_{\mathrm{AA}}$ associated with atomic orbitals on center A. If $\mathbf{P}_{\mathrm{AA}}$ is diagonalized (with respect to the associated overlap matrix $\mathbf{S}_{\mathrm{AA}}$) to give eigenvalues $n_i^{(\mathrm{A})}$ and eigenvectors $\mathbf{h}_i^{(\mathrm{A})}$

$$\mathbf{P}_{\mathrm{AA}}\mathbf{h}_i^{(\mathrm{A})} = n_i^{(\mathrm{A})}\mathbf{S}_{\mathrm{AA}}\mathbf{h}_i^{(\mathrm{A})} \qquad \text{(II.5)}$$

one expects an eigenvalue $n_i^{(\mathrm{A})} \approx 2$ for each (doubly-occupied) lone-pair orbital and $n_i^{(\mathrm{A})} \approx 1$ for each half-filled orbital available for covalent bonding. Similarly, if one diagonalizes the "2 × 2" submatrix $\mathbf{P}^{(\mathrm{AL})}$ (with associated overlap matrix $\mathbf{S}^{(\mathrm{AL})}$) (see eq II.6) to find the eigenvalues $n_i^{(\mathrm{AL})}$ and eigenvectors $\mathbf{h}_\mathrm{i}^{(\mathrm{AL})}$ (see eq II.7), one expects an additional eigenvalue $n_i^{(\mathrm{AL})} \approx 2$ for each (doubly-occupied) covalent bond between A and L, together with those (lone pairs) found previously in the separate atomic blocks $\mathbf{P}_{\mathrm{AA}}$ and $\mathbf{P}_{\mathrm{LL}}$. In practice, the near degeneracy of lone-pair and bond-pair eigenvalues may lead to significant mixing of the corresponding eigenvectors, but this may be avoided by "depleting" $\mathbf{P}^{(\mathrm{AL})}$ of lone-pair eigenvectors $\mathbf{h}_l^{(\mathrm{A})}$ found previously in the diagonalization of $\mathbf{P}_{\mathrm{AA}}$

$$\mathbf{P}^{(\mathrm{AL})} \equiv \begin{bmatrix} \mathbf{P}_{\mathrm{AA}} & \mathbf{P}_{\mathrm{AL}} \\ \mathbf{P}_{\mathrm{LA}} & \mathbf{P}_{\mathrm{LL}} \end{bmatrix} \qquad \text{(II.6)}$$

$$\mathbf{P}^{(\mathrm{AL})}\mathbf{h}_i^{(\mathrm{AL})} = n_i^{(\mathrm{AL})}\mathbf{S}^{(\mathrm{AL})}\mathbf{h}_i^{(\mathrm{AL})} \qquad \text{(II.7)}$$

$$\bar{\mathbf{P}}^{(\mathrm{AL})} \equiv \mathbf{P}^{(\mathrm{AL})} - n_l^{(\mathrm{A})}\mathbf{h}_l^{(\mathrm{A})}\mathbf{h}_l^{(\mathrm{A})\dagger} \qquad \text{(II.8)}$$

If there is a single bond between A and L, the depleted matrix $\bar{\mathbf{P}}^{(\mathrm{AL})}$ is expected to have a unique eigenvector $\bar{\mathbf{h}}_i^{(\mathrm{AL})}$ with approximate double occupancy ($\bar{n}_i^{(\mathrm{AL})} \approx 2$) (see eq II.9) and this

$$\bar{\mathrm{h}}_i^{(\mathrm{AL})} = \begin{bmatrix} \bar{\mathrm{h}}_l^{(\mathrm{A})} \\ \bar{\mathrm{h}}_a^{(\mathrm{L})} \end{bmatrix} \qquad \text{(II.9)}$$

may be chosen to represent the bond orbital between a directed hybrid $\bar{\mathbf{h}}_l^{(\mathrm{A})}$ on center A and the corresponding hybrid $\bar{\mathbf{h}}_a^{(\mathrm{L})}$ on center L. Since the hybrids found in this manner are generally nonorthogonal, it is necessary to symmetrically orthogonalize[27] these initial hybrids $\{\mathbf{h}_n^{(\mathrm{A})}, \bar{\mathbf{h}}_l^{(\mathrm{A})}, \bar{\mathbf{h}}_{l'}^{(\mathrm{A})} ...\}$ to obtain the final *natural* hybrid orbitals for each center.

In implementing this procedure, it is necessary to specify the minimal occupancy ($n_{\min}$) that will be accepted to constitute an electron "pair". In the applications reported here, this was taken to be

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$$n_{\min} = 1.9000$$

but typical bond occupancies ($n \approx 1.98$–2.00) made the precise value of this threshold immaterial, except in certain cases of apparent "resonance" (see below).

In summary, our procedure consists of the following steps: (i) find the density matrix $\mathbf{P}$ in a basis set of atomic orbitals and diagonalize each atomic subblock $\mathbf{P}_{AA}$ to find the lone-pair hybrid(s) on that center; (ii) for each pair of atoms, A,L, form the two-center density matrix $\mathbf{P}^{(AL)}$, eq II.6, and the associated matrix $\bar{\mathbf{P}}^{(AL)}$ "depleted" of any lone-pair eigenvectors as in (II.8) [each doubly-occupied ($n > n_{\min}$) eigenvector $\bar{\mathbf{h}}_l^{(AL)}$ of this matrix is decomposed as in (II.9) to give additional directed hybrids $\bar{\mathbf{h}}_l^{(A)}$ on center A]; (iii) symmetrically orthogonalize the hybrids found in steps i and ii to find the final *natural hybrids* $\{h_i\}$. Note that each step involves at most the diagonalization of a small submatrix of the full $\mathbf{P}$, so that the method is computationally quite efficient. Note also that if an insuffıcent number of two-center bond orbitals appear in the two-center density matrices of step ii, it becomes necessary to similarly examine *three*-atom blocks $\mathbf{P}^{(ALL')}$ for possible three-center bonds. In this way, the multicenter bonds of boranes and related compounds appear automatically in our procedure.

Our method for finding natural hybrids derives from an early suggestion by McWeeny,[28] who defined natural hybrids as the eigenvectors of the one-center blocks $\mathbf{P}_{AA}$, as in step i above. We have found, however, that such hybrids do not have directional properties appropriate to the formation of bonds to other atoms. An exception occurs for linear molecules, where one p orbital (say, p_z) of the central atom is chosen to lie along the molecular axis, so that the eigenvectors of $\mathbf{P}_{AA}$ necessarily consist of in-phase and out-of-phase linear combinations of s and p_z orbitals, pointed in the proper directions for linear bonds. However, for more general molecular geometries, the McWeeny hybrids bear little resemblance to those found by other methods.

III. Numerical Applications

Following the procedure described in section II, we calculated natural hybrid orbitals for a variety of molecules, making use of the INDO-SCF-MO approximation[29] to obtain the one-electron density matrix in each case. In the INDO approximation the basis AO's are implicitly orthonormal, so that the eigenvalue equation (II.7) is correspondingly simplified, and only the valence-shell electron density is considered. Unless otherwise specified, all calculations employed idealized bond lengths and angles as described by Pople and Gordon.[30]

To test whether the NHO's successfully incorporate the "best possible" aspect of the maximum-occupancy orbitals, we calculated the latter orbitals for a number of molecules (CH_4, NH_3, H_2O, CH_3F, NH_2F, C_2H_6, and C_2H_4) by a numerical optimization procedure.[31] In each case the hybridization coefficients were numerically adjusted to maximize the occupancy (II.3a) of the corresponding bond orbitals within a specified tolerance, and the resulting optimal hybrids were compared with those obtained directly by the NHO procedure. Table I shows the results for the three cases where slight differences (as large as 0.1% p character) were noted; in all other cases the NHO's agreed to the number of decimals given with the orbitals found numerically. The numerically optimized hybrids are subject to two difficulties: (i) incomplete convergence, when the hybrid occupancy is a very "flat" function of the adjustable coefficients and (ii) convergence to a local extreme, rather than to the desired global maximum. The latter problem was observed in some preliminary calculations on H_2O. The former problem seems to be responsible for the remaining small discrepancies in CH_3F and NH_2F (Table I), where the NHO's actually have slightly higher occupancy than do the incompletely converged numerical hybrids. We conclude that the NHO's satisfactorily satisfy the "maximum-occupancy" criterion to a high degree of accuracy but are more efficiently and reliably calculated.

Table I. Comparison of Maximum-Occupancy Hybrids with Natural Hybrid Orbitals[a]

		% hybrid p character[b]	
molecule	bond	maximum-occupancy hybrid	natural hybrid
CH_3F	CH	72.8	72.0
	CF	81.6	84.0
NH_2F	NH	76.1	76.6
	NF	87.5	86.0
$H_2C{=}CH_2$	CH	69.8	70.3
	CC(σ)	60.6	59.2
	CC(π)	100.0	100.0

[a] For those molecules where small differences in % p character (>0.1%) were found. [b] See ref 32.

Table II. Comparison of Natural Hybrid Orbitals (NHO'S) with Hybrids Determined by Other Methods[a]

			% hybrid p character[f]	
molecule	bond		other methods[d,e]	natural hybrid orbitals
CH_4	CH		75.0[d]	75.0
C_2H_6	CH		74.6[d]	75.8
	CC		76.1[d]	72.6
$H_2C{=}CH_2$	CH		68.5[d]	70.3
	CO(σ)		63.1[d]	59.2
$H{-}C{\equiv}C{-}H$	CH		55.6[d]	55.2
	CC(σ)		44.4[d]	44.8
cyclopropane, C_3H_6[b]	CH		71.4[d]	71.9
	CC		78.6[d]	77.8
NH_3	NH		76.9[e]	77.1
	n_N		69.3[e]	68.6
H_2O	OH		79.5[e]	81.8
	$n_O{}'$		70.4[e]	36.3
	$n_O{}''$		70.4[e]	100.0
norbornane, C_7H_{12}[c,g]	C_1H		71.3[d]	75.7
	C_2H		66.6[d]	77.7 (exo) 77.0 (endo)
	C_7H		72.6[d]	76.8
	$C_1{-}C_2$	C_1		73.8
		C_2		72.9
	$C_2{-}C_3$	C_2		72.5
		C_3		72.5
	$C_1{-}C_7$	C_1		76.5
		C_7	77.5[d]	73.2

[a] NHO results employ the idealized geometries of ref 30, except for cyclopropane and norbornane, where experimental geometries were used. Results labeled "other methods" employ experimental geometries. [b] Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* 1964, *17*, 538–543. [c] Chiang, J. F.; Wilcox, C. F.; Bauer, S. H. *J. Am. Chem. Soc.* 1968, *90*, 3149–3157. [d] Maximum-overlap criterion.[17b] [e] Maximum-localization criterion.[16] [f] See reference 32. [g]

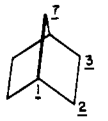

Table II shows the NHO's for a selection of molecules in which comparisons are possible with hybrids found by other methods. These alternative hybrids were often calculated for geometries slightly different from the idealized values used in all our NHO results, which leads to a certain portion of the observed discrepancies. Nevertheless, there is reasonable overall agreement in Table II between the NHO's and previous hybrids, with but few exceptions. The NHO's seem generally to ascribe somewhat higher p character to CH bonds throughout the series of hydrocarbons, reflecting perhaps a general tendency of INDO to exaggerate the electronegativity of H. A more conspicuous discrepancy is seen for the H_2O lone pairs, where the natural hybrids

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(as well as the numerical maximum-occupancy hybrids) suggest one pure[32] p and one $sp^{0.57}$ lone pair, whereas the procedure of ref 16 suggests symmetric lone pairs of 70.4% p character. These alternatives have similar occupancy, and one can judge from the similarity of the OH bond hybrids (79.5% vs. 81.8% p character) that the total wave functions for the two hybridizations would be similar. We return below to discuss the H_2O lone pairs in greater detail.

The cyclopropane molecule (C_3H_6) is particularly interesting in that no possible real[33] hybrids can point at the required 60° bond angles of the C_3 ring, and therefore some degree of "bent bonding" is necessary. Such bending could be minimized if the CC hybrids assumed pure p character, but the NHO analysis agrees with the Murrell-overlap criterion that nearly normal alkane-type $sp^{3.50}$ hybrids are employed. However, gross discrepancies are encountered in the case of the strained molecule norbornane (bicyclo[2.2.1]heptane) where, as shown in Figure 2, the CH hybrids of ref 17 seem to contain far less p character than do the corresponding NHO's. This discrepancy is particularly acute at the C_2 position, where the CH bond is reported to be an $sp^{2.00}$ hybrid in ref 17, whereas the NHO's are $sp^{3.48}$ (exo) or $sp^{3.35}$ (endo). Since the experimental HC_2H bond angle is somewhat *less* than tetrahedral, it seems unlikely that the trigonal $sp^{2.00}$ hybrid could satisfy a maximum-overlap criterion, and the disagreement may therefore be due to some error in calculating the maximum-overlap hybrids. With the exceptions noted above, we conclude that the NHO's agree to a reasonable extent with hybrids found by other methods and are generally consistent with chemical intuition.

Table III summarizes the NHO's for a variety of other small molecules and compares these with the "nominal" hybrids that would be expected from the classic valence rules. It should be emphasized that the "Lewis structures" shown in Table III are those obtained a priori by the NHO procedure. In each case we have also given the value of (cf. eq II.3b)

$$\rho^* = \sum_{\text{antibond orbitals } i} P_{ii} = \text{total antibond occupancy}$$

which measures the total occupancy of antibond orbitals for the chosen hybrids and is therefore a measure of the error in approximating the total wave function by a single "resonance structure" of doubly-occupied bond orbitals built from these hybrids. For a poor choice of hybrids (or for a molecule where no single resonance structure is adequate) the value of ρ^* increases; conversely, the improvement provided by the natural hybrids over the nominal hybrids is reflected in the smaller value of ρ^*_{natural} as compared to ρ^*_{nominal}. Note that while ρ^* can be reduced by an optimal choice of hybrids, there is generally an irreducible minimum value ($\approx \rho^*_{\text{natural}}$) which reflects the intrinsic role of antibonds in the wave function and cannot be made to vanish for any choice of the bond orbitals.

Entries **a**–**e** of Table III show the NHO p character for some diatomic molecules. The homonuclear diatomics A_2 show the predicted increase in p character of the σ_{AA} bond with increasing electronegativity of A, the F_2 bond being nearly pure p. As originally suggested by Moffitt,[34] the carbon σ-bond hybrid in $C{\equiv}O$ has far greater p character ($sp^{4.3}$) than the "nominal" sp description would suggest, and the corresponding nitrogen hybrid ($sp^{2.7}$) in $N{\equiv}N$ is also in substantial agreement with Moffitt's estimate. In contrast to the symmetrical "nominal" hybrid sp^n lone pairs, the natural lone pairs are found to be quite unsymmetrical, one having high s character (low energy, high occupancy) and the other(s) essentially pure p (although HF shows significant s character in two of its lone pairs). The sharp reduction of antibond density ($\rho^*_{\text{nominal}} \rightarrow \rho^*_{\text{natural}}$) in these molecules is almost entirely associated with this reorganization of lone pairs. One can see that the total antibond density is negligibly small (<0.001) in the diatomics, some 1–2 orders of magnitude less than the values typical of polyatomics, where vicinal bond–antibond interactions are possible.

Among the polyatomic molecules the peroxides HOOH (**g**) and FOOF (**h**) show a particularly dramatic reduction of antibond density with natural hybrid formation, far more than the 10–20% which is typical for other polyatomics. These changes are indicative of the strong deviations from nominal sp^3 bonding in these molecules. Somewhat less dramatic changes are indicated in HCN (**f**) and HNO_2 (**r**), but in most cases the nominal hybrids seem to do a reasonably good job in terms of their relatively high occupancy (compared to the presumed maximum-occupancy of the NHO's). The antibond density tends to be largest in molecules with low-lying π^* orbitals, as would be expected. Note that among molecules with formal π bonds, only formamide (**p**) exhibits significant "banana-bonding" character, the remaining molecules being well described by the conventional (σ,π) picture.

Table III contains many examples to illustrate Bent's Rule.[9] Thus, in compounds of the form CH_3–X, the CH hybrids show diminished p character with increasingly electronegativity of the nearest bonded atom of X[35] in the series –CN (**q**, $sp^{3.16}$), $-CH_3$ (Table II, $sp^{3.13}$), –H (Table II, $sp^{3.00}$), $-NH_2$ (**k**, $sp^{2.90}$), $-OCH_3$ (**n**, $sp^{2.81}$), –OH (**i**, $sp^{2.79}$), and –F (Table I, $sp^{2.57}$). Similarly the oxygen hybrid of an oxygen double bond can be seen to vary systematically in the series formaldehyde (**j**, $sp^{2.10}$), glyoxal (m, $sp^{2.25}$), formamide (**p**, $sp^{3.32}$), nitrous acid (r, $sp^{4.03}$), and O_2 (**b**, $sp^{6.49}$). As suggested by Bent,[9] the p character of the CH bond of acetylene ($sp^{1.25}$) exceeds that of HCN ($sp^{1.14}$) and the p character of a vinylic CH bond ($H_2C{=}CH_2$, $sp^{2.37}$) exceeds that of an aldehydic ($H_2C{=}O$, $sp^{1.95}$). These trends are in turn consistent with observed trends in experimental data on which Bent's Rule rests.[9] It is also noteworthy (see, e.g., i, **k**, n, **o**) that bond hybrids trans to lone pairs tend to have greater p character.

The NHO procedure was noted to fail in two cases: CO_2 and HCOOH. In CO_2 the occupancy of the second "lone pair" on each oxygen atom was only 1.6258, well below the acceptance threshold, and the computer program subsequently identified three two-center bonds of high occupancy on each CO, leading to a miscount of the total number of orbitals (since an additional antibond orbital is attributed to each two-center bond). This points to a significant contribution from "resonance structures" of the form

$$:\underset{\cdot\cdot}{\ddot{O}}{-}C{\equiv}O: \leftrightarrow :O{\equiv}C{-}\underset{\cdot\cdot}{\ddot{O}}:$$

which prevent the determination of a single set of NHO's for a unique Lewis structure.[36] The failure of the NHO procedure for formic acid seems to have a similar origin.[37] We subsequently attempted NHO analysis of the benzene molecule and found that it failed similarly. Such failures are to be anticipated when multiple resonance structures are important; indeed, one might think of adapting the NHO procedure to provide a numerical criterion for the occurrence of significant "resonance" in a given molecule.

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[32] In all our calculations, hybrids beyond $sp^{99.99}$ were arbitrarily rounded to "pure p" orbitals. Thus, some of the orbitals listed in the tables as "100.00% p character" may in fact have small (<1%) s contributions.

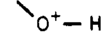
[33] Coulson, C. A.; White, R. J. *Mol. Phys.* **1970**, *18*, 577–588.

[34] Moffitt, W. *Proc. Roy. Soc. London, Ser. A* **1949**, *196*, 524–539.

[35] This series suggests that the electronegativity of the directly bonded atom, rather than the "group electronegativity" of X, affects hybrid p character most directly. Thus, although CN behaves in certain respects as a better electron-withdrawing group than F (as judged, for example, by Hammett σ constants), the C hybrid toward CN in CH_3CN is more like that of a typical CC bond than a CF bond.

[36] Although one could accept a second O "lone pair" of abnormally low occupancy and thereby produce a single Lewis structure, the resulting antibond density ρ^* is so high as to make this description of doubtful utility. Thus, for the nominal $O{=}C{=}O$ structure one finds $\rho^*_{\text{nominal}} = 0.9057$, with approximately 0.42 electron in each π^* orbital! The idea that resonance structures contribute importantly to the ground state of CO_2 is discussed by: Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, N.Y., 1960; p 267.

[37] In this case, $\rho^*_{\text{nominal}} = 0.2937$, the principal contribution being the occupancy (0.1194) of the π^*_{CO} antibond, as would be associated with a resonance structure of the form



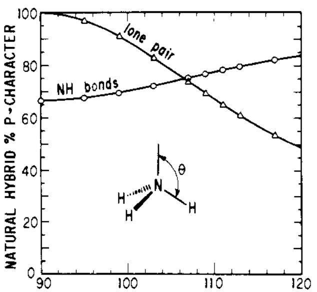


Figure 1. Change in hybridization of NH_3 with change in the pyramidal angle θ (see inset), as measured by the percentage of p character of the natural hybrid orbitals.

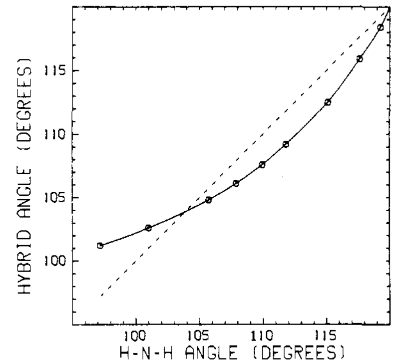


Figure 2. Comparison of the angle HNH between nuclei with the separation angle between the natural hybrids, illustrating the imperfect "orbital following" during the NH_3 umbrella inversion.

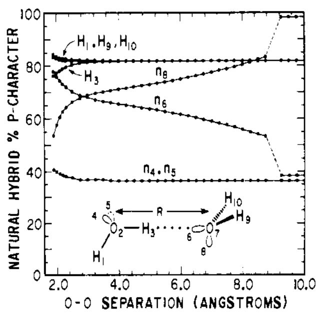


Figure 3. Hybridization changes in the water dimer as a function of O–O separation, showing the rehybridization of natural lone pairs from the inequivalent forms of the separated molecules to the "rabbit ears" of the H-bonded complex (see text). Each molecule is assumed to have idealized tetrahedral geometry (R_{OH} = 0.96 Å), with a linear O_2–H_3···O_7 hydrogen bond (see inset), and each curve is labeled by the ligand to which the corresponding natural hybrid is directed.

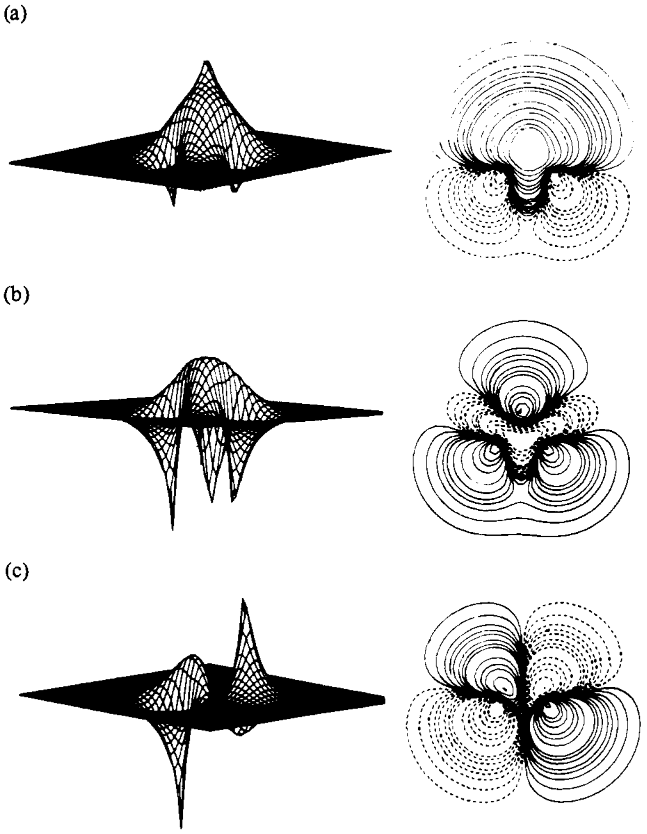


Figure 4. Natural three-center bonds and antibonds for diborane, as seen in surface and contour plots. Positions of the BHB nuclei can be determined from the positions of the three peaks in plot b: (a) three-center bond orbital, $\sigma_{BHB} \approx 3^{-1/2}(h_{B_1} + s_H + h_{B_2})$; (b) three-center antibond orbital, $\sigma_{BHB}'^* \approx 6^{-1/2}(2s_H - h_{B_1} - h_{B_2})$; (c) three-center antibond orbital, $\sigma_{BHB}''^* \approx 2^{-1/2}(h_{B_1} - h_{B_2})$.

We finally describe three additional examples which further illustrate the applications of the NHO analysis:

The first example concerns the changes of hybridization accompanying the "umbrella inversion" of the ammonia molecule. Figure 1 shows the natural hybrid orbital p character for this case, illustrating the changes in nitrogen lone pair and bond hybrids with change of bond angle. As simple valence theory would suggest, the lone pair rehybridizes from the pure p character of the planar transition state to approximate sp^3 character of the equilibrium pyramid, while the p character of the N–H bond hybrids simultaneously increases. Figure 2 compares the angle between the bonding natural hybrids and the HNH angle, showing that the NHO's do not perfectly follow the nuclei through the inversion motion.[38] As indicated by this figure, the hybrids move away from planarity more rapidly than do the nuclei near the planar transition state but fall "behind" the nuclei for HNH angles much smaller than tetrahedral. The "bending" of the bonds is minimized at an intermediate angle (~104°) where the directions of the hybrids and the nuclei coincide. This suggests that it would be interesting to investigate to what extent the natural hybrids, as calculated for an arbitrary nonequilibrium geometry, indicate the directions in which nuclei distort to achieve their equilibrium arrangement.[39]

The second example concerns the interactions of water molecules to form a hydrogen-bonded dimer.[40] The changes of hybridization accompanying this interaction are shown in Figure 3 with the idealized geometry depicted in the figure inset. As previously remarked, the isolated water molecule shows two inequivalent lone pairs, one having 36.3% ($sp^{0.57}$) p character and the other essentially pure p, as seen in the large R limit in Figure 3. However, as the water molecules begin to interact, there is a dramatic rehybridization of the lone pairs of the right-hand ("donor") molecule to form approximately equivalent "rabbit ears" lone pairs of $\sim sp^{2.1}$ character near $R \approx 3$ Å. As shown in Figure 3, at very large separation (~9 Å), there is an abrupt change in lone-pair hybridization which seems to be associated with a degeneracy in occupancy involving two distinct choices of hybridization. At this distance it becomes more favorable to form directional hybrids than to leave the lone pairs in their nearly atomic configuration, and a "crossing" of occupation numbers for the alternative hybrids occurs. Because of the finite word length of the computer (double-precision Univac 1110), it was not possible to numerically resolve this near degeneracy in the vicinity of the crossing, the hybrids being numerically indeterminate of the interval 8.75–9.25 Å. At somewhat smaller distances

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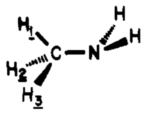
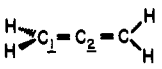
[38] See, e.g.: Cohan, N. V.; Coulson, C. A. *Trans. Faraday Soc.* **1956**, *52*, 1163–1172.

[39] Although one might assume (see, e.g., ref 38) that the equilibrium positions of the nuclei would be such as to minimize bond bending, we have found that this is not the case. Thus, when NH_3 is given its (INDO) optimum geometrical parameters (R_{NH} = 1.069 Å, $\angle_{HNH}$ = 106.39°), the angle (103.91°) between the bonding natural hybrids is still about 2.5° smaller than that between the nuclei.

[40] Horn, J. S.; Weinstock, R. B.; Weinhold, F., University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-624 (unpublished).

Table III. Natural Hybrid Orbitals for Various Molecules


II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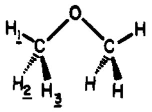
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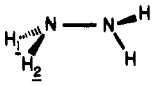
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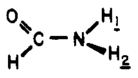
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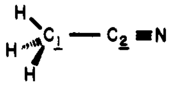
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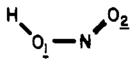

VIII

molecule	bond	center	% natural hybrid p character^a	total antibond density	
				ρ^*_{nominal}	ρ^*_{natural}
(a) N≡N	NN(σ)	N	72.8 ($sp^{2.68}$)	0.1102	0.0000
	NN(π',π'')	N	100.0 (p)		
	n_N	N	27.0 ($sp^{0.37}$)		
(b) O=O (singlet)	OO(σ)	O	86.6 ($sp^{6.49}$)	0.7292	0.0000
	OO(π)	O	100.0 (p)		
	n_O'	O	13.0 ($sp^{0.15}$)		
	n_O''	O	100.0 (p)		
(c) F_2	FF	F	96.5 ($sp^{27.68}$)	0.2173	0.0000
	n_F'	F	3.8 ($sp^{0.04}$)		
	n_F''	F	100.0 (p)		
	n_F'''	F	100.0 (p)		
(d) HF	FH	F	83.9 ($sp^{5.23}$)	0.0131	0.0000
	n_F'	F	39.4 ($sp^{0.65}$)		
	n_F''	F	78.7 ($sp^{3.69}$)		
	n_F'''	F	98.1 ($sp^{50.93}$)		
(e) C≡O	CO(σ)	C	81.2 ($sp^{4.32}$)	0.1711	0.0009
	CO(π',π'')	C	100.0 (p)		
	n_C	C	20.0 ($sp^{0.25}$)		
	OC(σ)	O	64.8 ($sp^{1.84}$)		
	OC(π',π'')	O	100.0 (p)^b		
	n_O	O	36.3 ($sp^{0.57}$)		
(f) HC≡N	CH	C	53.3 ($sp^{1.14}$)	0.0673	0.0285
	CN(σ)	C	46.8 ($sp^{0.88}$)		
	CN(π',π'')	C	100.0 (p)		
	NC(σ)	N	69.6 ($sp^{2.29}$)		
	NC(π',π'')	N	100.0 (p)		
	n_N	N	30.6 ($sp^{0.44}$)		
(g) HOOH	OH	O	82.2 ($sp^{4.61}$)	0.1599	0.0083
	OO	O	92.1 ($sp^{11.65}$)		
	n_O'	O	25.9 ($sp^{0.35}$)		
	n_O''	O	100.0 (p)		
(h) FOOF	FO	F	94.4 ($sp^{16.99}$)	0.5231	0.0461
	n_F'	F	9.9 ($sp^{0.11}$)		
	n_F''	F	95.6 ($sp^{21.85}$)		
	n_F'''	F	100.0 (p)		
	OF	O	93.9 ($sp^{15.32}$)		
	OO	O	93.0 ($sp^{13.20}$)		
	n_O'	O	13.0 ($sp^{0.15}$)		
	n_O''	O	100.0 (p)		
(i) CH_3OH (I)	CH_1	C	73.2 ($sp^{2.73}$)	0.0854	0.0602
	CH_2, CH_3	C	74.0 ($sp^{2.84}$)		
	CO	C	78.9 ($sp^{3.73}$)		
	OC	O	79.5 ($sp^{3.87}$)		
	OH	O	83.5 ($sp^{5.06}$)		
	n_O'	O	37.1 ($sp^{0.59}$)		
	n_O''	O	100.0 (p)		
(j) $H_2C=O$	CH	C	66.1 ($sp^{1.95}$)	0.1184	0.1103
	CO(σ)	C	67.7 ($sp^{2.10}$)		
	CO(π)	C, O	100.0 (p)		
	OC(σ)	O	73.2 ($sp^{2.73}$)		
	n_O'	O	27.0 ($sp^{0.37}$)		
	n_O''	O	100.0 (p)		
(k) CH_3NH_2 (II)	CH_1	C	74.9 ($sp^{2.99}$)	0.0835	0.0738
	CH_2, CH_3	C	74.4 ($sp^{2.90}$)		
	CN	C	76.3 ($sp^{3.22}$)		
	NC	N	74.6 ($sp^{2.94}$)		
	NH	N	78.6 ($sp^{3.67}$)		
	n_N	N	68.3 ($sp^{2.15}$)		
(l) $CH_2=C=CH_2$ (III)	CH	C	69.4 ($sp^{2.27}$)	0.2308	0.2155
	C_1C_2(σ)	C_1	61.1 ($sp^{1.57}$)		
	C_1C_2(π)	C_1, C_2	100.0 (p)		
	C_2C_1(σ)	C_2	50.0 ($sp^{1.00}$)		

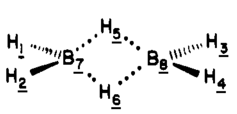
Table III (*Continued*)

molecule	bond	center	% natural hybrid p character[a]	total antibond density	
				ρ^*_{nominal}	ρ^*_{natural}
(m) $(HC{=}O)_2$	CH	C	68.4 ($sp^{2.16}$)	0.2890	0.2652
	CO(σ)	C	69.2 ($sp^{2.25}$)		
	CO(π)	C, O	100.0 (p)		
	CC	C	37.7 ($sp^{1.65}$)		
	OC(σ)	O	73.2 ($sp^{2.73}$)		
	n_O'	O	27.0 ($sp^{0.37}$)		
	n_O''	O	100.0 (p)		
(n) CH_3OCH_3 (IV)	CH_1	C	73.8 ($sp^{2.81}$)	0.1530	0.1360
	CH_2, CH_3	C	73.8 ($sp^{2.82}$)		
	CO	C	78.6 ($sp^{3.68}$)		
	OC	O	80.7 ($sp^{4.17}$)		
	n_O'	O	38.7 ($sp^{0.63}$)		
	n_O''	O	100.0 (p)		
(o) N_2H_4 (V)	NH_1	N	77.3 ($sp^{3.40}$)	0.0890	0.0518
	NH_2	N	78.4 ($sp^{3.64}$)		
	NN	N	81.8 ($sp^{4.28}$)		
	n_N	N	63.2 ($sp^{1.72}$)		
(p) $HCONH_2$ (VI)	CH	C	66.6 ($sp^{1.99}$)	0.2824	0.2631
	CO(σ)	C	76.9 ($sp^{3.32}$)		
	CO(π)	C	89.2 ($sp^{8.25}$)		
	CN	C	67.4 ($sp^{2.07}$)		
	OC(σ)	O	82.0 ($sp^{4.55}$)		
	OC(π)	O	92.6 ($sp^{12.51}$)		
	n_O'	O	25.4 ($sp^{0.34}$)		
	n_O''	O	100.0 (p)		
	NH_1	N	78.3 ($sp^{3.61}$)		
	NH_2	N	79.4 ($sp^{3.85}$)		
	NC	N	72.1 ($sp^{2.58}$)		
	n_N	N	70.2 ($sp^{2.36}$)		
(q) $CH_3C{\equiv}N$ (VII)	CH	C	76.0 ($sp^{3.16}$)	0.1699	0.1311
	C_1C_2	C_1	72.1 ($sp^{2.59}$)		
	C_2C_1	C_1	51.5 ($sp^{1.06}$)		
	CN(σ)	C	48.5 ($sp^{0.94}$)		
	CN(π',π'')	C, N	100.0 (p)		
	NC(σ)	C	69.4 ($sp^{2.27}$)		
	n_N	N	30.6 ($sp^{0.44}$)		
(r) HNO_2 (VIII)	OH	O	83.5 ($sp^{5.06}$)	0.4088	0.1837
	O_1N	O_1	86.2 ($sp^{6.25}$)		
	n_O'	O_1	30.1 ($sp^{0.43}$)		
	n_O''	O_1	100.0 (p)		
	NO_1	N	88.6 ($sp^{7.76}$)		
	NO_2(σ)	N	80.1 ($sp^{4.03}$)		
	NO_2(π)	N, O_2	100.0 (p)		
	n_N	N	31.5 ($sp^{0.46}$)		
	O_2N	O_2	83.2 ($sp^{4.96}$)		
	n_O'	O_2	18.7 ($sp^{0.23}$)		
	n_O''	O_2	100.0 (p)		

[a] See ref 32. [b] The oxygen hybrid for the second "π bond" actually has about 1.8% s character ($sp^{53.97}$).

($3\ \text{Å} \lesssim R \lesssim 8\ \text{Å}$) the directional lone pairs of the donor $O_7H_9H_{10}$ molecule become progressively more equivalent, whereas the remaining bond and lone-pair hybrids are scarcely affected. Finally (below $R \approx 3$ Å), as a strong H-bond interaction begins to occur, the acceptor O_2H_3 hybrid (pointed toward the incipient donor n_6) acquires noticeably higher s character while the donor lone pair n_6 continues to gain in p character. The final H bond ($R_{\text{eq}} \approx 2.5$ Å) seems to be associated with a localized n–σ^* "charge-transfer" interaction between the donor lone pair n_6 and the acceptor antibond $\sigma^*_{O_2H_3}$.[40] As can be seen in Figure 3 the remaining O_2H_1, O_7H_9, and O_7H_{10} hybrids remain essentially equivalent during H-bond formation, serving only as "spectators" to the principal n_6–$\sigma^*_{O_2H_3}$ interaction and undergoing only weak secondary changes in hybridization. The natural hybrids thus point strongly to the *localized* nature of the charge-transfer interaction in H-bond formation.[41]

The third example illustrates the automatic recognition of three-center bonds in hydrogen-bridged compounds such as diborane (B_2H_6), taken to have the idealized tetrahedral geometry shown in structure A. When one attempts to extract a natural



A, $R_{B_7H_5} = 1.37$ Å; $R_{B_7H_1} = 1.19$ Å

two-center function for the B_7H_5 pair by the procedure of section II, the occupation ($n_{B_7H_5} = 1.3934$) is found to be significantly below that associated with a normal electron-pair bond (e.g., $n_{B_7H_1} = 1.9835$). However, the analogous procedure applied to the three-center $B_7H_5B_8$ block leads to a three-center bond orbital of double occupancy ($n_{B_7H_5B_8} = 2.0000$). This natural three-center orbital is depicted in contour and surface plots in Figure 4a. The participating boron NHO's have 77.2% p character ($sp^{3.38}$), pointing at the bridging H atom ($H_5B_7H_6$ angle = 109.47°; angle between B_7H_5 and B_7H_6 hybrids = 109.42°). Each such three-center bond orbital is associated with *two* antibond orbitals, which are depicted in parts b and c of Figure 4. We emphasize that the various two- and three-center electron-pair bond orbitals appear automatically in our procedure, without any previous reference to the number or location of "chemical bonds" in the molecule.

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(41) We noted similar results for the $H_2O \cdots C_2H_4$ complex, where the (acceptor) H_2O rehybridizes in a manner very similar to $O_2H_1H_3$ above, while the (donor) ethylene rehybridizes from inequivalent (σ,π) double bonds to an unsymmetrical set of "banana bonds".

IV. Conclusion

Using only the information contained in the (exact or approximate) first-order density matrix, we have described a procedure for extracting general hybrids, polarization parameters, and bond orbitals and thereby constructing an a priori "Lewis structure" for a given molecule.[42] The method is applicable at any level of ab initio or semiempirical theory and is computationally efficient, involving only the diagonalization of small matrices and a symmetric orthogonalization. The method seems to apply (when a single resonance structure is dominant) to a variety of bonding situations, including molecules with lone pairs, multiple bonds, strained rings and "bent bonds", hydrogen bonds, and three-center bonds. The resulting *natural hybrids* appear to be in good agreement with hybrids determined by other methods and to be consistent with known empirical trends such as those summarized in Bent's Rule and with chemical intuition. Moreover, they appear to closely resemble the "best possible" hybrids, as defined by maximal occupancy of the one-electron density matrix.

Although the NHO's possess a number of desirable features for bond orbital studies and are in a certain sense optimal for this purpose, one should note a certain disadvantage inherent in their use. Since the NHO's change continuously with the molecular environment, they are not generally transferable from one molecule to another. For the same reason the NHO's do not necessarily form a suitable fixed basis set for the comparison of one molecule with another or for the analysis of changes within a single molecule. For the latter purposes the "nominal" hybrids retain a distinct conceptual advantage, particularly when the antibond density associated with the two sets of hybrids is similar.

The illustrative numerical applications of this paper were carried out at the semiempirical INDO level of approximate SCF–MO theory. It would be desirable to obtain corresponding ab initio (SCF or CI) natural hybrids for a number of the systems considered here, in order to compare the effects of various approximations at the level of individual atomic hybrids, polarization parameters, and occupancy. We hope to report such studies at a later date.

Acknowledgment. We thank Dr. Graham Doggett for calling our attention to McWeeny's paper and Professor J. O. Hirschfelder for support. Financial support from the National Science Foundation (Grant CHE76-22760) is also gratefully acknowledged.

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[42] A Fortran implementation of this procedure, part of the general bond orbital package for INDO–LCBO–MO calculations (BONDO), is being submitted to the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana 47405.

Electronic Control of Stereoselectivity. 4. Effects of Neighboring Fused Bicyclic Frameworks on the Stereochemical Outcome of Diels–Alder Cycloadditions to Cyclopentadiene Rings[1]

Michael C. Böhm,[2a] Richard V. C. Carr,[2b] Rolf Gleiter,*[2c] and Leo A. Paquette*[2b]

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210, the Institut für Organische Chemie der Technischen Hochschule, D-6100 Darmstadt, West Germany, and the Institut für Organische Chemie der Universität, D-6900 Heidelberg, West Germany. *Received January 18, 1980*

Abstract: The stereochemistry of Diels–Alder cycloadditions to tricyclo[5.2.1.$0^{2,6}$]deca-2,5-diene (**1**), tricyclo[5.2.1.$0^{2,6}$]deca-2,5,8-triene (**2**), and tricyclo[5.2.2.$0^{2,6}$]undeca-2,5,8-triene (**3**) has been investigated with various dienophiles. In the reactions involving **1** and **2**, single products were obtained in each instance, and unambiguous structural proof was obtained for kinetically favored stereospecific bond formation from the endo surface of the diene moiety. As concerns **3**, the additions were stereoselective only, with exo attack now being favored. These observations cannot be attributed to steric factors, for the behavior of **1** and **3** would be countrasteric in that event. Rather, the stereochemical phenomena are best rationalized in terms of σ orbital mixing with the π_s diene orbital, such interactions serving to tilt the diene orbitals disrotatorily with resultant minimization of the level of antibonding interaction on the endo face of **1** and **2** relative to the exo face. Theory predicts a reduction in stereoselectivity for **3** as is seen.

The norbornane ring system, a focal point of physical organic chemistry for several decades, continues to evade a universally acceptable interpretation of its unique and often complex chemical reactivity. The capture by norbornyl cations of various nucleophiles is widely recognized to occur preferentially from the exo side.[3–5] Similarly, addition reactions to norbornene double bonds proceed with essentially complete exo stereoselection, except in certain cases where C_7 substituents interfere.[6] The first phenomenon was originally attributed to presumed nonclassical characteristics of the cationic species.[7] With the advent of Brown's more recent studies,[8] it has become clear that high percentages of exo product do not require a bridged ion explanation. The demise of the nonclassical electronic interpretation has caused torsional[9] and steric effects[10] to be considered seriously. However,

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[2] (a) Institut für Organische Chemie Darmstadt. (b) The Ohio State University. (c) Institut für Organische Chemie Heidelberg.

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