JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 97, NUMBER 3 FEBRUARY 5, 1975

Semiempirical Natural Orbitals. CNDO/2–NO and INDO–NO Analysis of Charge Densities, Dipole Moments and Rotational Barriers in Small Molecules

Peter V. Alston,[1a,b] **Donald D. Shillady,***[1a] **and Carl Trindle**[1c]

Contribution from the Chemistry Departments, Virginia Commonwealth University, Richmond, Virginia 23284, and the University of Virginia, Charlottesville, Virginia. *Received November 24, 1973*

Abstract: Semiempirical natural orbitals have been obtained for several small molecules using the configuration interaction algorithm of Reeves. The CNDO/2, INDO, and, in some cases, the CNDO/S parameter systems are used with up to 40 single and pairwise doubly excited configurations for an iterative pseudo-natural orbital procedure. Generally the atomic charges become more nearly neutral, dipole moments decrease, and rotational barriers improve upon natural orbital CI treatment. The CNDO/2 parameters seem best overall of the three methods. It is shown how "orthonormal-resonance (←O→) structures" and natural orbital occupation numbers can be used to represent the results of a CI wave function in a nonsubjective fashion analogous to traditional VB resonance structures. "Orthonormal resonance analysis" of the natural orbital CI wave functions is given for formaldehyde and formic acid.

It has been many years since the molecular orbital (MO) philosophy of Hückel,[2a] Mulliken,[2b] Roothaan,[3] Parr,[4] and many others seemed to assume dominance over the early valence bond (VB) approach of Heitler and London[5] and Pauling,[6] at least in terms of a first-order approach to molecular electronic structure. On the other hand, many concepts invoked in organic reaction mechanisms[7] are heavily dependent upon resonance ideas and on hybridization schemes inherent in the VB formalism. Only recently have the MO interpretations of Woodward and Hoffmann[8] really stimulated the application of MO interpretations as a first resort rather than invoking a variety of resonance structures for a given reaction pathway. The apparent reason for the ascendancy of one-electron MO methods has always seemed to be relative computational ease, ease of parameterization of MO methods, and especially an easy interpretation of electron delocalization.

In view of the fact that the VB computational procedure has been developed to a high degree of automation by Pauling,[6] Boys and Cook,[9] Cooper and McWeeny,[10] and Shull,[11] and even published as an algorithm by Reeves,[12] it is surprising that so little semiempirical work has been attempted to apply conventional VB interpretations to molecular electronic phenomena. A number of excellent *ab initio* VB calculations[13-16] have appeared, but we know of only one BeH_2[17] calculation where semiempirical VB methods were tested recently. With the fast computers available today, most of the previous objections to VB methodology are gone and it seems desirable to consider VB methods within the framework of CNDO- or INDO-type semiempirical methods. We wish to report some results of applying the Reeves algorithm to these semiempirical wave functions in a way which incorporates substantial portions of both VB and MO philosophies in an attempt to express a more useful approach which largely salvages the advantages of both MO and VB techniques and discards their individual disadvantages.

Natural Orbitals

A very important mathematical concept which allows one to employ configuration interaction and still make interpretations in terms of one-electron charge densities and bond orders is that of natural orbitals pioneered by Löwdin[18] and Kutzelnigg[19] and applied with great success by Bender and Davidson[20] and Schaeffer.[21] The transformation of the one-electron part of a CI wave function into what Löwdin[18] calls a first-order density matrix gives one essentially a multiconfigurational-bond-order matrix while the eigenfunctions of the density matrix also give occupational numbers of these orbitals which indicate contributions from configurations other than the dominant configuration. This analysis necessarily follows the CI step.

The Reeves algorithm[12] is particularly interesting because it considers configuration interaction for an arbitrary spin system using techniques which follow directly from the early VB analysis of Pauling[6] with the important difference that Reeves restricts his method to *orthonormal* functions. As VB schemes are generally described, the configurations are constructed from nonorthogonal atomic orbitals on different atoms. The use of orthonormalized linear combinations of basis orbitals greatly simplifies the computation in Reeves' method and it also means that when SCF orbitals are used, this restricted VB algorithm becomes numerically identical with MO configuration interaction. However, we wish to reemphasize that the Reeves routine is completely dependent on the use of VB techniques such as superposition of Rumer[23] diagrams and identification of "islands," "chains," and "links" in the superposition pattern for a Hamiltonian matrix element between two configurations. Thus this routine is really a restricted (to orthonormal functions) VB algorithm that becomes identical with MOCI when SCF orbitals are used. Since it is advantageous to use SCF orbitals anyway, why should we mention the VB ancestry of the Reeves algorithm? We believe that *interpretation of the wave function in terms of "orthonormal-resonance interactions"* may hold more promise than do interpretations couched in terms of many-body interactions, because of historical dependence on resonance structures in chemistry. Of course, orthonormal resonance (VB resonance restricted to orthonormal linear combinations of basis functions) is not exactly the same as pure VB resonance due to the inclusion of orthogonalizing portions of many different basis functions, but this delocalization is considered to be one of the prime advantages of the MO method! Thus we wish to analyze a MOCI wave function in terms of "orthonormal-resonance" contributions in the hope that the pure VB concepts are only slightly modified. Let us modify the pure VB symbolism $A \leftrightarrow B$ where structures A and B have a nonzero Hamiltonian matrix element $\langle A|\mathbf{H}|B\rangle$ to that of $A' \longleftarrow O \longrightarrow B'$, where $\langle A'|\mathbf{H}|B'\rangle \neq 0$ and A' and B' are configurations constructed from orthonormal linear combinations of basis functions. Under this operational definition the special case of SCF singly-excited configurations would be said to have zero orthonormal resonance with the SCF ground state due to Brillouin's theorem[25] while doubly-excited SCF configurations would be found to be in orthonormal resonance with the SCF ground state to varying extents. Thus with slight modifications the use of VB-like ideas may be interfaced directly with delocalized one-electron orbital MO-like interpretations by using the connecting idea of natural orbitals. It is apparent that the natural orbital analysis within any given *ab initio* or semiempirical framework is superior to either a VB or MO approach alone within the same computational framework because of the multiconfigurational advantage over single configurational MO methods and the retention of one-electron "orbitals" while incorporating resonance effects.

If the ground state of a molecular electronic system is determined by a linear combination of spin-projected configurations (orthonormal bonded structures) that yields the lowest energy variationally, the coefficients C_i can be used to create a multiconfigurational first-order density matrix $\rho(1)$

$$|\Psi_{\text{CI}}\rangle = \mathbf{P}\sum_i C_i\Phi_i;\ \langle\Psi_{\text{CI}}|\mathbf{H}|\Psi_{\text{CI}}\rangle = E_{\text{min}} \tag{1}$$

using the same spin-projection operator **P**. In general the total n-particle density operator is given by $|\Psi_{\text{CI}}\rangle\langle\Psi_{\text{CI}}|$. We have slightly modified the Reeves algorithm to obtain only the one-electron portion of this general form by terminating the projection operation after the first-order density matrix (the "one matrix") has been obtained. We denote this abbreviated procedure by $\rho(1) = |\Psi_{\text{CI}}(1)\rangle\langle\Psi_{\text{CI}}(1)|$. In this form we also note that this is a spinless first-order density matrix. The matrix form of $\rho(1)$ can be diagonalized to yield occupation numbers N_i and a transformation matrix **T** which can be applied to the orbital coefficient matrix **A** in terms of atomic orbitals. The new **A′** matrix then contains pseudo-natural orbitals which are then used to construct

$$\rho(1)\mathbf{T} = N_i(\text{diagonal})\mathbf{T};\ \mathbf{TA} = \mathbf{A}' \tag{3}$$

new, improved Φ_i configurations. In actual practice $\rho(1)$ is projected by **P** in the molecular orbital basis and must be converted to $\rho'(1)$ in the atomic orbital basis to be used as a bond order or population matrix as for one-electron properties. Note that the N_k occupation numbers need not be integers and that one must sum over all linear combinations of

$$\begin{gathered}\rho_{ij}'(1) = \sum_k N_k a_{ik} a_{jk}^* \\ \Psi_i(\text{NO}) = \sum_j a_{ij}\phi_j;\ \mathbf{A}' \longrightarrow a_{ij}\end{gathered} \tag{4}$$

atomic orbitals ϕ_j since all natural orbitals $\Psi_i(\text{NO})$ can be partially occupied. Generally, those occupied orbitals which would be assigned exactly 2 electrons in an SCF calculation will have N_k values slightly less than 2.0, say 1.96, while orbitals which would be unoccupied virtual orbitals in an SCF calculation will typically have occupation numbers less than 0.1 in the MOCI expansion. Of course, some configuration utilizing a given orbital must be present in the expansion for that orbital to have a nonzero occupation number.

$$\mathbf{S}^2|\Psi_{\text{CI}}\rangle = s(s+1)\hbar^2|\Psi_{\text{CI}}\rangle;\ \mathbf{S}_z|\Psi_{\text{CI}}\rangle = s_{\text{max}}\hbar|\Psi_{\text{CI}}\rangle \tag{2}$$

Computational Methods

The calculations to be described were carried out using an extensively modified copy of CNINDO, Q.C.P.E. program No. 141 written by Pople and Dobosh and completely documented by Pople and Beveridge.[24] The published algorithm of Reeves[12] was translated into Fortran and substituted for the closed-shell SCF routine, while the open-shell SCF routine was modified to do either open- or closed-shell SCF calculations. We have allowed for up to 40 configurations constructed from the SCF eigenvectors. In the case of open-shell SCF calculations the α spin electron eigenvectors are used. The necessary two-electron integrals computed over linear combinations of basis functions are obtained very rapidly using the zero differential overlap (ZDO) approximation and then corrected in the case of INDO calculations by contributions on each atom from the same formulas used in the INDO-SCF procedure.[24]

The Reeves algorithm projects only the highest S_z component of a given orthonormal valence bond configuration, but the procedure is entirely automatic for any spin multiplicity and the results are eigenvectors of the total spin operator S^2 as well as S_z. Only a slight modification was needed to use that part of Reeves' algorithm which spin projects one-electron operators to create the first-order density matrix after the interaction between configurations has been diagonalized, the lowest energy eigenvector being the ground state. We trust that by starting with SCF eigenvectors, the use of only 40 configurations is less of a severe approximation than if we had started from core-hybrid orbitals as in the pure VB approach. In any event, practical considerations forced us to limit the configurations to 40.

The first-order density matrix is diagonalized in place to prevent permutation of orbital types on successive iterations and the eigenvector matrix is applied to the SCF-MO coefficient matrix to correct them (only slightly in most cases) to pseudo-natural orbitals. These orbitals are then used to set up another interaction matrix and the process is cycled until the energy of the lowest state converges to 10^{-7} hartrees. This usually required only a few iterations and often only two were needed, indicating rapid convergence.

Table I. Calculated Energies (au)

Compd	CNDO/2	CNDO/2–NO	INDO	INDO–NO
Ethylene[a]	−17.067959	−17.090835	−16.561898	−16.593965
Formaldehyde[a]	−26.832467	−26.862468	−25.739057	−25.776375
Ammonia[a]	−13.872562	−13.885158	−13.361991	−13.383332
Water[b]	−19.868065	−19.879147	−19.013620	−19.032132

[a] Geometry from D. D. Shillady, F. P. Billingsley, and J. E. Bloor, *Theor. Chim. Acta*, **21**, 1 (1971). [b] Geometry from H. F. Schaeffer and C. F. Bender, *J. Chem. Phys.*, **55**, 1720 (1971).

In selecting configurations a perturbation philosophy was used in that we used a 5,4,3,2,1 rule wherein the highest occupied SCF orbital was excited to the lowest 5 virtual orbitals, etc., in the hope that these nearby energy levels would be more likely to contribute to the ground state than much higher energy levels. Additional excitations thought to be important were then added to bring the total to 40 configurations. In each case we followed Green's[25] suggestion and for every double excitation (pairwise) we included the corresponding single excitation unless it was symmetry forbidden. Thus we only improved on the SCF orbitals and prevented overemphasis of pairwise double excitations. Split pair excitations were neglected as nonessential for closed-shell singlet bonding.

Since we have no previous numerical work to check against, we rely on the fact that our CI routine correctly gives exactly the same energy as the SCF procedure for the dominant configuration when constructed from SCF orbitals, although the algorithm is substantially different in organization, and the fact that all single excitations from the dominant configuration have zero interaction matrix elements with the dominant configuration, satisfying Brillouin's theorem[26] for SCF orbitals. These computations were carried out in double precision arithmetic on a IBM 370/145.

One very satisfying benefit from using the multiconfigurational first-order density matrix is that one can merely substitute it for the SCF population matrix in those routines such as for the dipole moment and charge densities which are set up to evaluate one-electron properties from the population matrix. Thus our dipole moments and charge densities are easy to compare, within the same ZDO framework, to the corresponding SCF-CNDO/2 or -INDO values. This should be general for any spin-free one-electron operator.

In this preliminary work we have used primarily Pople's[24] standard parameters and theoretical repulsion integrals for spherical orbitals. We also have provided for other paramaters and semiempirical integrals. We plan to investigate the use of the MINDO[27] approximations in the future, but this present work should serve to indicate the usefulness of the semiempirical natural orbital (SNO) method within the limitations of a given semiempirical framework.

Charge Densities in Small Molecules

In order to evaluate the SNO method we selected several molecules small enough to carry out a configuration interaction including all single and all paired-double excitations within our limit of 40 orthonormal VB structures. For the molecules shown in Table I it was possible to use symmetry considerations to eliminate those configurations that would not interact with the principal SCF structure for single excitations even on successive NO iterations where Brillouin's theorem no longer obtains. For ethylene we neglected three double excitations from the lowest σ orbital to the highest unoccupied orbitals in order to limit the number of structures to 40. There are many other possible configurations, especially of the multiple excitation type, but for these the electronic energy required to excite the electrons using a simple first-order perturbation philosophy seemed prohibitive and justified their neglect within a limit of 40 orthonormal structures in the configuration interaction.

Table I shows the computed valence shell energies for the four methods we have used. The energy lowering due to configuration interaction is only 0.02 au typically, but this is about 12.55 kcal/mol so that rotational barriers and conformational energy dependence could be entirely different with and without CI. These relatively large energy changes prompted us to investigate the effect of SNO–CI on a number of different types of rotational barriers.

In Table II we present the ZDO atom charges from the single and multiconfigurational wave functions. The results for ethylene indicate that the SNO results are dependent on the method used in the initial MO–SCF calculation, being a refinement based on coarser approximations. This situation is somewhat analogous to cases where attempts have been made to examine correlation effects[28] within a semiempirical framework. One understands from the beginning that the overall results are largely determined by the parameters involved, and yet one hopes that trends in smaller effects can be observed relative to a particular parametric scheme. Clearly one must be cautious in making conclusions based on semiempirical schemes alone, but when suggestive models are needed and computer facilities are restricted, the search for improved interpretation should be valid, particularly in the gap between the pure VB and MO methods. In this spirit we note that water, ammonia, formaldehyde, and

Table II. Electron Distribution (ZDO)

Compd	Atom	CNDO/2	CNDO/2–NO	INDO	INDO–NO
Ethylene	C	−0.0261	−0.0261	+0.0068	+0.0065
	H	+0.0131	+0.0130	−0.0034	−0.0033
Formaldehyde	C	+0.2186	+0.1900	+0.3362	+0.2933
	O	−0.1838	−0.1530	−0.2329	−0.1906
	H	−0.0174	−0.0185	−0.0517	−0.0513
Ammonia	N	−0.2446	−0.2387	−0.2637	−0.2519
	H[a]	+0.0815	+0.0787	+0.0879	+0.0829
	H	+0.0815	+0.0800	+0.0879	+0.0845
Water	O	−0.2849	−0.2742	−0.3345	−0.3142
	H	+0.1425	+0.1371	+0.1673	+0.1571

[a] The tendency toward a unique H charge was strongest on the first CI iteration. On successive iterations the H charges became more nearly equal, but not completely. This is one slight disadvantage of limiting the number of configurations but the unique charge effect is more characteristic of an oddfold rotational axis than it is of a true resonance effect.

Table III. Calculated Dipole Moments (D)

Compd	CNDO/2	CNDO/2-NO	INDO	INDO-NO	Exptl
Ethylene	0.0	0.0	0.0	0.0	0.0
Formaldehyde	1.9007	1.6628	1.8973	1.6040	2.33[a]
Ammonia	1.9735	1.9520	1.8758	1.8390	1.47[b]
Water	2.1451	2.1043	2.1814	2.1191	1.82[b]

[a] W. Huttner, M. K. Lo, and W. H. Flygare, *J. Chem. Phys.*, **48,** 1206 (1968). [b] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

even ethylene indicate significant changes almost always from a slightly ionic situation to a more covalent situation with both positive and negative net charges decreasing in magnitude. This trend is reinforced in Table III where we see that the dipole moments decrease upon SNO-CI treatment, and in the case of formaldehyde that shift is in the wrong direction while the values for water and ammonia improve slightly. Clearly this casts doubts on the validity of the CNDO/2 or INDO standard parameterization in a multiconfigurational environment, but also offers hope that a new set of parameters may be found which represent pure configurations better, rather than try to match a compromise of many resonant forms in a single determinantal model. Another possibility is that the level of sensitivity in the SNO-CI method is limited to energy effects less than those which can be assigned to uncertainties in the semiempirical parameters.

Rotational Energy Barriers

We next considered a number of weak bonding situations to test the SNO-CI method. We selected a number of different types of barrier interactions for which both experimental and *ab initio* results are available for comparison.

In Table IV we see that in a hydrogen bond barrier both the CNDO/2-NO and INDO-NO method yield significant improvement for the cis isomer of formic acid, with INDO-NO somewhat better. The nonhydrogen bonded trans isomer is also greatly improved in energy but we do not know the experimental barrier here and the INDO-NO results are greater than a good *ab initio* calculation. In this case there are π resonance effects in the trans isomer as well as hydrogen bonding in the cis isomer and the CI with a total of 40 single and pairwise double excitations gives a marked improvement over both the CNDO/2- and INDO-SCF results.

A more subtle type of rotational barrier is encountered in acetaldehyde. Evidently a weak hydrogen bond is set up between the lone pair of nonbonded electrons on oxygen and a methyl hydrogen in the eclipsed conformation. In both methods the CI improvement is slight but in the right direction and the CNDO/2-NO is better. A π-π^* resonance interaction in the carbonyl group is also important here.

In borazane we have a molecule which has a large dipole moment and is fully saturated. In this case only slight improvement was obtained using the SNO-CI method. Here there are few competing low-energy resonant structures and the single SCF determinant evidently does as well as the semiempirical methods allow without needing many other configurations.

In the cases of propene and the two isomers of fluoropropene (cis and trans) we have a weak bonding interaction between a methyl hydrogen and either another hydrogen or fluorine atom in the eclipsed conformation of the methyl group. The rotational barrier is small, but the CNDO/2-NO result is better than some very good *ab initio* calculations in all three cases. The INDO-NO result for *cis*-fluoropropene seems to overemphasize the hydrogen bonding to the fluorine atom. Again a π-π^* resonance interaction is

Table IV. Calculated Energies (au) and Barriers (kcal/mol)[g]

Compd	CNDO/2	CNDO/2-NO	INDO	INDO-NO	*Ab initio*	Exptl
cis-Formic acid	−45.305189	−45.323578	−43.364645	−43.386343		
90° Formic acid	−45.297772	−45.312772	−43.354992	−43.370853		
trans-Formic acid	−45.302013	−45.320020	−43.361026	−43.382129		
Barrier (cis-90°)	4.654	6.780	6.057	9.719	13.0[a]	13.4[b]
Barrier (trans-90°)	2.661	4.548	3.786	7.075	4.9[a]	
Acetaldehyde (H eclipsing O)	−35.541607	−35.558783	−34.191084	−34.211605		
Acetaldehyde (H eclipsing H)	−35.540523	−35.557221	−34.189923	−34.210210		
Barrier	0.743	0.980	0.728	0.876	1.09[c]	1.16[d]
Borazane (eclipsed)	−20.169911	−20.176933	−19.567839	−19.580406		
Borazane (staggered)	−20.172777	−20.179826	−19.570740	−19.583334		
Barrier	1.798	1.815	1.820	1.837	2.9332[e]	
Propene (staggered)	−25.772336	−25.783526	−25.010962	−25.025780		
Propene (eclipsed)	−25.774247	−25.785927	−25.012938	−25.027968		
Barrier	1.199	1.507	1.234	1.373	1.25[f]	1.98[f]
trans-Fluoropropene (eclipsed)	−52.761826	−52.772539	−50.692180	−50.705261		
trans-Fluoropropene (staggered)	−52.759802	−52.769806	−50.690024	−50.702509		
Barrier	1.270	1.715	1.353	1.727	1.34[f]	2.20[f]
cis-Fluoropropene (eclipsed)	−52.763848	−52.774335	−50.693906	−50.707376		
cis-Fluoropropene (staggered)	−52.762141	−52.772658	−50.692244	−50.705095		
Barrier	1.071	1.053	1.043	1.431	1.07[f]	1.06[f]

[a] M. E. Schwartz, E. F. Hayes, and S. Rothenberg, *J. Chem. Phys.*, **52,** 2011 (1970). [b] D. L. Bernitt, K. O. Hartman, and I. C. Hisatsune, *ibid.*, **42,** 3553 (1965). [c] R. B. Davidson and L. C. Allen, *ibid.*, **54,** 2828 (1971). [d] R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *ibid.*, **26,** 1695 (1957). [e] W. E. Palke, *ibid.*, **56,** 5308 (1972). [f] E. Scarzafava and L. C. Allen, *J. Amer. Chem. Soc.*, **93,** 311 (1971). [g] We have used 27.21 eV/au and 23.059 (kcal/mol)/eV.

Table V. Calculated Dipole Moments (D)

Compd	CNDO/2	CNDO/2-NO	INDO	INDO-NO	*Ab initio*	Exptl
cis-Formic acid	0.8900	0.9451	0.9763	1.0648	1.241[a]	1.415[b]
Acetaldehyde (H eclipsing O)	2.5478	2.4361	2.5404	2.3932		2.69[c]
Borazane (BH_3-NH_3) (staggered)	6.4589	6.4453	6.4895	6.4607	6.673[d]	5.01[e]
Propene (eclipsed)	0.3844	0.3781	0.2646	0.2748		0.366[c]
trans-Fluoropropene (eclipsed)	1.7387	1.7143	1.6823	1.6572		
cis-Fluoropropene (eclipsed)	1.6817	1.6346	1.7181	1.6614		1.46[c]

[a] M. E. Schwartz, E. F. Hayes, and S. Rothenberg, *J. Chem. Phys.*, **52**, 2011 (1970). [b] H. Kim, R. Keller, and W. D. Gwinn, *ibid.*, **37**, 2748 (1962). [c] "Handbook of Chemistry and Physics," 49th ed, R. C. Weast Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1969, E-67. [d] W. E. Palke, *J. Chem. Phys.*, **56**, 5308 (1972). [e] R. W. Parry, W. A. D. C. Technical Report 59-207, University of Michigan, 1959, gives an improvement over the value of 4.92 D previously reported by J. R. Weaver, S. G. Shore, and R. W. Parry, *J. Chem. Phys.*, **29**, 1 (1958).

important here.

Since we took care to use the same geometries as the *ab initio* calculations in each case we conclude that the SNO-CI method compares favorably with the *ab initio* results for rotational barriers. On our, relatively slow, IBM 370/145 the full SNO-CI treatment including the SCF step and three natural orbital iterations averaged about 60 min. We estimate that the (10s, 10p) Whitten[29] basis used by Scarzafava and Allen[30] would require about 50 hr using our own *ab initio* programs.[31,32] It seems that the CNDO/2-NO method gives slightly better agreement with experiment than the *ab initio* methods which are currently feasible; the INDO-NO option is not as satisfactory using standard parameters.

In Table V we report the computed dipole moments for the molecules in the study of rotational barriers. In these computations the limit to 40 configurations means that the SNO-CI treatment is less complete for these molecules than for the molecules in Table III. Thus the changes in dipole moment are almost all small and generally in the direction of a more covalent, less ionic, lower dipole electronic structure. However, the results for *cis*-formic acid are very interesting. Note that the SNO-CI treatment improved the dipole moment in the right direction in spite of the fact that the same parameters predicted the wrong trend in the dipole of formaldehyde. By far the most important configuration in the formaldehyde CI calculation, other than the SCF configuration, was the π-π^* double excitation with a coefficient of 0.161 in the CNDO/2-NO ground state. The effect of this configuration is to make the carbon and oxygen charges more nearly equal while slightly decreasing the bond strength of the carbonyl bond; the σ bond structure gains slightly in strength in the C–H bond region. Since this seems reasonable to us chemically, we suspect that the dipole of formaldehyde should decrease upon CI treatment, but that the semiempirical parameters have made it too low in the SCF step. We later tried the Jaffe[33] parameters to try to remedy this.

The CNDO/S method described by Jaffe, *et al.*,[33] was added to our program as an option. Formaldehyde and formic acid were then treated by the SNO-CI method in the CNDO/S parameter system. In Table VI we show that the CNDO/S dipole moments are higher than either INDO or CNDO/2 values and that the CNDO/S-NO dipoles are quite a bit lower than their CNDO/S counterparts. In eq 5

$$\left.\begin{aligned}\Psi_\pi &= -0.658\Phi_{2p_z}(\mathrm{C}) - 0.753\Phi_{2p_z}(\mathrm{O});\\ N_\pi &= 1.949\\ \Psi_{\pi*} &= 0.753\Phi_{2p_z}(\mathrm{C}) - 0.658\Phi_{2p_z}(\mathrm{O});\\ N_{\pi*} &= 0.051\end{aligned}\right\}\ \text{CNDO/2–NO}$$

$$\left.\begin{aligned}\Psi_\pi &= -0.611\Phi_{2p_z}(\mathrm{C}) - 0.792\Phi_{2p_z}(\mathrm{O});\\ N_\pi &= 1.940\\ \Psi_{\pi*} &= 0.792\Phi_{2p_z}(\mathrm{C}) - 0.611\Phi_{2p_z}(\mathrm{O});\\ N_{\pi*} &= 0.060\end{aligned}\right\}\ \text{CNDO/S–NO} \tag{5}$$

we see that the π and π^* natural orbitals are really not very different for the two methods. The main difference between the CNDO/2 and CNDO/S dipoles seems to occur in the σ bonds. From Table II the (O, C, H) charges are (−0.1838,

Table VI. Results with Jaffe Parameters[a]

	Formaldehyde		
CNDO/S energy, au	−13.777119	CNDO/S dipole, D	3.4484
	−13.688948		3.4491
CNDO/S–NO energy, au	−13.803285	CNDO/S–NO dipole, D	3.0050
	−13.712543		2.9941

	Cis	90°	Trans
	Formic Acid		
CNDO/S energy, au	−20.620190	−20.692096	−20.730783
	−20.457303	−20.529638	−20.568610
CNDO/2-NO energy, au	−20.632733	−20.707090	−20.743781
	−20.470125	−20.544998	−20.581916
CNDO/S dipole, D	1.8877	3.8758	5.24788
	1.8802	3.8685	5.23728
CNDO/S–NO dipole, D	1.7309	3.5991	5.0406
	1.7212	3.5868	5.0314
(Cis-90°) barrier, kcal/mol	45.116	46.654	
	45.386 (SCF)	46.978 (NO)	
(Trans-90°) barrier, kcal/mol	24.273	23.021	
	24.452 (SCF)	23.164 (NO)	

[a] Upper values using Mataga repulsion integrals.[44] Lower values using Clarke repulsion integrals.[45]

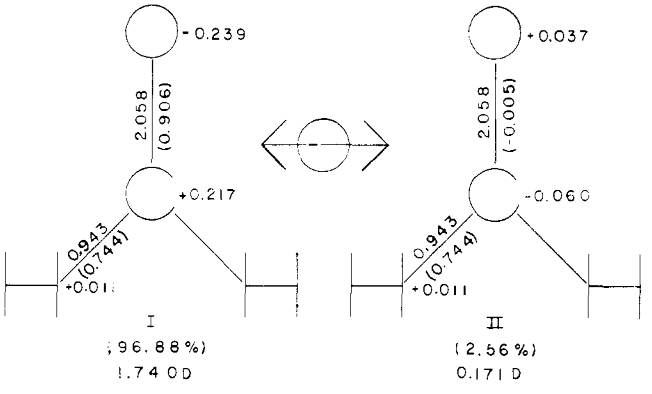


Figure 1.

+0.2186, −0.0174) for CNDO/2 and (−0.1530, +0.1900, −0.0185) for CNDO/2-NO while we find them to be (−0.3701, +0.2322, +0.0689) for CNDO/S and (−0.3067, +0.1794, +0.0636) for CNDO/S-NO. Since even the occupation numbers N_π and N_{π^*} are about the same for CNDO/2-NO and CNDO/S-NO we conclude that the main fault in the CNDO/2-NO dipole is caused by too much electron density on H in the CNDO/2-SCF step.

Since we have already observed that the CI algorithm we have used differs from a pure VB approach only in that orthonormal linear combinations of atomic orbitals are used to construct the configurations, we suggest that the orthonormal resonance structures shown in Figure 1 represent the main components of the CNDO/2-NO-CI wave function. In order to arrive at a nonsubjective analysis of the SNO-CI results, we have automated our description by computing ZDO dipole moments, Mulliken overlap populations, Mulliken gross atomic charges,[34] Wiberg-Trindle bonds indices,[35-37] and the square of the CI coefficient in the ground state of the five most important orthonormal resonance structures. The Wiberg-Trindle bond indices have been shown by one of us[36] to permit the partitioning of a determinant of molecular orbitals into valence bond components. The simplicity of the bond index analysis rests on the assumption of zero differential overlap in the atomic basis[38] so that VB structures within a MO determinant can be unambiguously resolved. Nonorthogonal atomic basis calculations can always be cast into ZDO form using eq 6

$$S_{ij} = \int \phi_i^* \phi_j d\tau; \quad S^{-1/2}SS^{-1/2} = 1;$$
$$S^{-1/2}A_{ZDO} = A_N; \quad A_{ZDO} = S^{1/2}A_N \qquad (6)$$

and conversely ZDO results can be deorthogonalized for Mulliken population analysis (using overlap) and Mulliken charges q_a.[39] The orbitals i and j are understood to belong

$$\text{B.I. (W-T)}_{ab} = \sum_i \sum_j \left(\sum_k N_k a_{ik}^* a_{jk} \right)^2 \qquad (7)$$

$$\text{O.P. (M)}_{ab} = \sum_i \sum_j 2 \sum_k N_k a_{ik}^* a_{jk} S_{ij} \qquad (8)$$

$$q_a = Z_a - \left(\sum_i \sum_k N_k a_{ik}^* \sum_j a_{jk} S_{ij} \right) \qquad (9)$$

to atoms a and b, respectively, N_k values are 2, 1, or 0 and Z_a is the effective nuclear charge of atom a.

The Wiberg-Trindle bond indices are necessarily positive and reflect the amount of charge participating in a given interaction; they do not give a direct indication whether an interaction is net bonding or antibonding. In contrast, the Mulliken populations reflect the strength of a bond and yield atomic charges somewhat more informative than the ZDO charges.[39] In Figures 1 and 2 we show the deorthogonalized net atomic charges and bond indices with the overlap populations in parentheses. Together, eq 6–9 can characterize each configuration in a CI-NO computation. The N_k values are determined by assigning all the electrons to a given structure according to the integer values 2, 1, or 0 of the pure configuration. The corresponding quantities for the total ground state can also be obtained using eq 6–9 with the noninteger N_k values from eq 3.

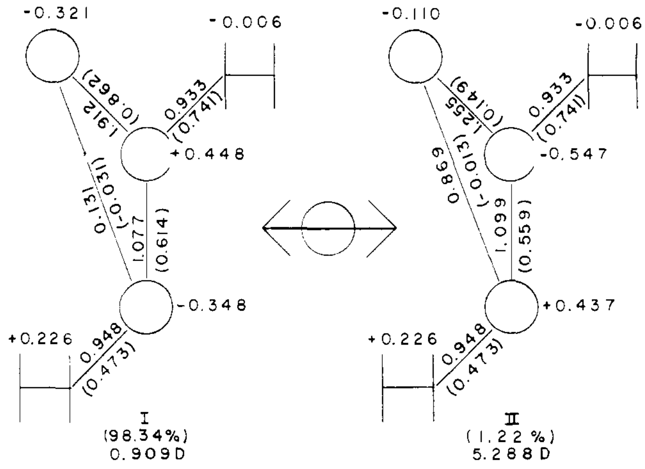


Figure 2.

The use of the bond index in multiconfigurational wave functions involves some subtleties. For example, in formaldehyde we see that the π–π^* double excitation greatly reduces the dipole moment of the dominant configuration by reversing the C and O charges and introducing antibonding character between C and O. One could say C and O achieve near neutrality here by eliminating charge transfer in the π bond. The C–O bond index is the same in I and II because the square of the cross term in eq 5 is the same in both cases. We would then resolve structure II into the same (π) valence bond structures as we find in structure I, but we would find a different weighting of ionic structures. Recalling that both the CI and a valence bond computation attempt to account for electron correlation in the C–O π bond, and that the π bond correlation is poorly described in the first NO configuration, we would expect that an analysis of the first NO configuration into VB structures would show an overemphasis of ionic structures. This was found in the allyl cation[36] and is a direct result of the incorrect dissociation behavior of a single-determinantal MO (NO here) wave function, of which the most familiar example is H_2. Since the admixture of a π^* double excitation produces a multiconfigurational wave function with proper dissociation behavior insofar as the π orbital is concerned (the CO σ orbital is not properly described until a σ double excitation is incorporated, but this was found to be only a small effect in our SNO-CI results), the $(\pi^*)^2$ configuration must contain ionic structures tending to cancel the ionic structures in the dominant configuration. Since the σ structures are virtually invariant between structures I and II in Figure 1, we conclude by inspection of charges that structure II contains more of the structure $H_2C^-O^+$ than does structure I and structure I contains more of structure $H_2C^+O^-$ than does structure II. Admixture of II tends to reduce the overestimate of the importance of structure $H_2C^+O^-$ typical of I. Our semiempirical results indicate that II is only a 2.56% contribution to the ground state, however, and structures I and II together make up 99.44% of the total ground state. If we were to describe the system as it dissociates to $^3CH_2$ and ^3O, the cancellation of ionic VB structures effected by admixture of doubly excited NO configurations would become far more extensive.

Each NO configuration corresponds in a unique way to a collection of VB structures, presuming a ZDO basis. In the CI, admixture of excited configurations to improve the description of the ground state can be viewed as an awkward way to mix *sets* of VB structures. We suggest that the set of bond indices typical of a configuration, which contain all information on the content of VB structures implicit in the configuration, be referred to as an "orthonormal-resonance structure" and that the mixing of configurations in the MO–CI be called "orthonormal-resonance interaction" and denoted ←O→. This conversion will correspond closely to VB usage when a configuration is dominated by a single VB structure, as is the case[37] for localized ground state species. Where the single configuration encompasses numerous pure VB structures we would be spared the encumbrance of large numbers of structures, but allowed to recover those structures if necessary. Also, one could carry out only a small CI between the few important orthonormal-resonance structures and obtain nearly as good a result as a large MO–CI.[40]

The ability to conveniently represent the results of a configuration interaction calculation in a way that is both accurate in terms of natural orbitals and analogous to traditional valence bond resonance structures should be of considerable utility in the language of chemistry. We note the recent work by Graovac, *et al.*,[41] and that by Whangbo and Lee[42] where considerable effort was made to express chemical bonding in terms of resonance between specific types of VB structures in a way which is not only semiquantitative but also has a great appeal to chemical intuition. Alewood, *et al.*,[43] have also recently pointed out a need for a way to express a physical interpretation of configuration interaction wave functions. We suggest that orthonormal-resonance structures with their CI coefficients and the natural orbitals with their population numbers can satisfy chemical intuition as well as give mathematical definition of CI wave functions. Although we are using semiempirical methods here, the ←O→ notation is equally applicable to even the most accurate *ab initio* wave functions.

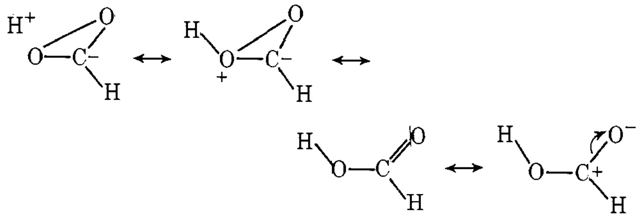
Let us consider *cis*-formic acid using the orthonormal resonance point of view. In the CNDO/2-NO-CI calculation the main configuration other than the SCF-like dominant configuration is a double excitation from the dominant configuration. In eq 10 we show the CNDO/2-NO natural π and π^* orbitals. The occupation number of the π^* orbital

$$\begin{aligned}
\Psi_\pi &= -0.673\Phi_{2\mathrm{P}_z}(\text{acid O}) + 0.304\Phi_{2\mathrm{P}_z}(\text{C}) + \\
&\qquad 0.675\Phi_{2\mathrm{P}_z}(\text{keto O}) \\
N_\pi &= 1.976 \\
\Psi_{\pi*} &= +0.248\Phi_{2\mathrm{P}_z}(\text{acid O}) - 0.766\Phi_{2\mathrm{P}_z}(\text{C}) + \\
&\qquad 0.592\Phi_{2\mathrm{P}_z}(\text{keto O}) \\
N_{\pi*} &= 0.026
\end{aligned} \tag{10}$$

(0.026) is very small but the orbital clearly shows an electron density shift from the acid oxygen to the carbon atom, while leaving the keto oxygen only slightly changed. Note that the orbital shows an in-phase bonding interaction between the two oxygen atoms while the carbon p orbital is antibonding with respect to both oxygen atoms.

In Figure 2 the total overlap population between the two oxygen atoms suggests negligible interaction, but the Wiberg–Trindle bond index shows almost a full single bond in the second orthonormal-resonance structure and the carbon and acid-oxygen charges change dramatically. We are reminded that the bond index measures the amount of charge participating in an interaction, while the overlap population measures the strength of the interaction. In eq 4 there is a large one-matrix element between the oxygens of 0.90 in the ZDO basis, but when this is weighted by the through-space overlap integral the overlap population is very small. To the extent that overlap allows, II shows a bonding tendency between the oxygen atoms in the π plane with some small antibonding effects in the σ plane. This leads to an increase in the ZDO dipole moment and a slight energy stabilization due to delocalization in the three-membered ring. As in formaldehyde, CI does essentially nothing to the σ bonds and since the orthonormal-resonance interaction is predominantly π, it is evidently not a small effect in that it is able to outweigh deficiencies in the parameters determining the σ bonds. We also conclude that the concurrent use of the bond indices and overlap populations is much more revealing than either value used separately. In structure I the 0–0 line is hardly needed and would be suppressed except for comparison with II.

We believe the SNO-CI method shows its value in that while the orthonormal-resonance structures are somewhat cluttered, only a few are needed compared to many true VB structures. *Qualitatively* one can also eliminate many possible VB structures after examining the orthonormal-resonance structures and postulate a few key structures as shown below.



some analogous true VB structures

Conclusions

It should be quite clear that natural orbitals and orthonormal resonance analysis of CI wave functions accomplishes considerable consolidation of chemical concepts. (1) The natural orbitals are one-electron orbital functions *a la* MO methods and they are the most rapidly convergent orbitals in a CI sense.[18] (2) Historical concepts in bonding theory[2-12] are merged and survive only slightly modified so that a bench chemist can analyze accurate CI wave functions using chemical intuition and need not resort to nonchemical (*i.e.*, electron correlation or many-body theory) concepts which are accurate but often foreign to the powerful analog minds of chemists. (3) The orthonormal resonance structures are nonsubjective and are mathematically defined; their accuracy and that of the natural orbitals are limited only by basis size, CI size, and, in our case, parametric approximations. These same limitations are common to any orbital computation. We submit that eq 1–4 and 6–9 define a nonsubjective analysis of chemical bonding. A single line between atom pairs with the bond index (eq 7) written along the line with the overlap population (eq 8) in parentheses describes a chemical "bond." Mulliken net charges (eq 9) written near each symbol indicate the amount of "unbonded" charge on each atom. The square of the CI coefficient (eq 1) from the ground state for each pure orthonormal resonance structure is converted to per cent composition of this structure and the symbolism A′ ←O→ B′ denotes $\langle A'|H|B'\rangle \neq 0$. The extent of the CI step depends on practical considerations but need not be totally complete using the iterative natural orbital approach. Both ZDO and nonorthogonal basis set effects are analyzed and both MO and VB techniques are used. We suggest that bond lines with indices less than 0.5 be suppressed and that SCF orbitals are the most efficient starting estimates of the natural orbitals.

Finally we note that the CNDO/2-NO-CI parametric scheme does a pretty good job of estimating rotational barriers in small molecules. The INDO-NO-CI results are less good and the CNDO/S parameters are not useful for calculating rotational barriers (Table VI). In cases where the SCF process very nearly produces the dominant configuration, the CNDO/2-NO-CI will offer little improvement, but where alternate low-energy configurations are available (delocalization) the natural orbital CI should offer improved electronic structure interpretations.

Acknowledgment. We wish to thank Dr. Richard Grove, Director of the V.C.U. Computer Center, and his Systems Programmer, Mr. David Brydon, for their cooperation in using the V.C.U. IBM 370/145 for the computations described above. P.V.A. also thanks the Texaco Corp. for a graduate fellowship and Professor Ray Ottenbrite for many discussions and research training. Finally we thank the referees for lively discussion and several very helpful and constructive suggestions, particularly in distinguishing between MO-CI and VB-CI techniques.

References and Notes

(1) (a) Virginia Commonwealth University; (b) Texaco Graduate Fellow, 1971–1973; (c) University of Virginia.
(2) (a) E. Hückel, *Z. Phys.*, **70**, 204 (1931); (b) R. S. Mulliken, *Phys. Rev.*, **32**, 186 (1928).
(3) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(4) R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N.Y., 1964.
(5) W. Heitler and F. London, *Z. Phys.*, **44**, 455 (1927).
(6) L. Pauling, *J. Chem. Phys.*, **1**, 280 (1933).
(7) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N.Y., 1959.
(8) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(9) S. F. Boys and G. B. Cook, *Rev. Mod. Phys.*, **32**, 285 (1960).
(10) I. L. Cooper and R. McWeeny, *J. Chem. Phys.*, **45**, 226 (1966).
(11) H. Shull, *Int. J. Quantum Chem.*, **3**, 523 (1969).
(12) C. M. Reeves, *Commun. ACM* (*Ass. Comput. Mach.*), **9**, 276 (1966).
(13) J. F. Harrison and L. C. Allen, *J. Mol. Spectrosc.*, **29**, 432 (1969).
(14) M. Rubenstein and I. Shavitt, *J. Chem. Phys.*, **51**, 2014 (1969).
(15) W. J. Hunt, P. J. Hay, and W. A. Goddard, *J. Chem. Phys.*, **57**, 738 (1972).
(16) C. Peterson and G. V. Pfeiffer, *Theor. Chim. Acta*, **26**, 321 (1972).
(17) R. G. A. Maclagan and G. W. Schnuelle, *J. Chem. Phys.*, **55**, 5431 (1971).
(18) P. O. Löwdin, *Phys. Rev.*, **97**, 1474 (1955).
(19) W. Kutzelnigg, *Theor. Chim. Acta*, **1**, 327, 343 (1963).
(20) C. F. Bender and E. R. Davidson, *Phys. Rev.*, **183**, 23 (1969).
(21) H. F. Schaeffer, "The Electronic Structure of Atoms and Molecules," Addison-Wesley, Reading, Mass., 1972.
(22) F. L. Pilar, "Elementary Quantum Chemistry," McGraw-Hill, New York, N.Y., 1968, p 370.
(23) G. Rumer, *Nachr. Ges. Wiss. Gottingen, Math.-Phys. Kl., Fachgruppe 3*, 337 (1932).
(24) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N.Y., 1970.
(25) S. Green, *J. Chem. Phys.*, **54**, 827 (1971).
(26) J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. 1, Electronic Structure of Molecules, McGraw-Hill, New York, N.Y., 1963, Appendix **4**.
(27) N. C. Baird and M. J. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969).
(28) O. Sinanoğlu and H. O. Pamuk, *J. Amer. Chem. Soc.*, **95**, 5435 (1973).
(29) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).
(30) E. Scarzafava and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 311 (1971).
(31) C. Trindle and D. D. Shillady, *J. Amer. Chem. Soc.*, **95**, 703 (1973).
(32) J. A. Kroll and D. D. Shillady, *J. Amer. Chem. Soc.*, **95**, 1422 (1973).
(33) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 1807, 4050 (1968); *ibid.*, **58**, 2238 (1973).
(34) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).
(35) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).
(36) C. Trindle, *J. Amer. Chem. Soc.*, **91**, 219 (1969).
(37) C. Trindle and O. Sinanoğlu, *J. Amer. Chem. Soc.*, **91**, 853 (1969).
(38) G. Doggett, *J. Chem. Soc. A*, 229 (1969).
(39) D. D. Shillady, F. P. Billingsley, and J. E. Bloor, *Theor. Chim. Acta*, **21**, 1 (1971).
(40) H. Shull and P. O. Löwdin, *J. Chem. Phys.*, **23**, 1565 (1955).
(41) A. Graovac, I. Gutman, M. Pandic, and N. Trinajstic, *J. Amer. Chem. Soc.*, **95**, 6267 (1973).
(42) M. H. Whangbo and I. Lee, *J. Amer. Chem. Soc.*, **93**, 2330 (1971).
(43) P. F. Alewood, P. M. Kazmaier, and A. Rauk, *J. Amer. Chem. Soc.*, **95**, 5466 (1973); particularly their footnotes 46 and 54.
(44) N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (*Frankfurt am Main*), **13**, 140 (1957).
(45) D. T. Clarke and J. W. Emsley, *Mol. Phys.*, **12**, 365 (1967).

Nonempirical Calculations on the Conformation and Hyperfine Structure of the Nitroxide and Ketyl Groups. Consequences of Out-of-Plane Bending on Hyperfine Interactions

Yves Ellinger,[1a,b] Robert Subra,*[1b] André Rassat,[1b] Jérôme Douady,[1c] and Gaston Berthier[1c]

Contribution from the Laboratoire de Chimie Organique Physique, Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, and C.I.S.I., Cedex 85, F 38041 Grenoble, France, and Laboratoire de Chimie, Ecole Normale Supérieure de Jeunes Filles, F 92120 Montrouge, France. *Received January 28, 1974*

Abstract: Nonempirical calculations of the ground-state energy and hyperfine coupling constants of the isoelectronic H_2NO and H_2CO^- radicals are performed using the spin-restricted SCF method and first-order perturbation theory. It is shown that the nitroxide functional group does not possess a well-defined intrinsic geometry, in agreement with experiment. The equilibrium geometry found for the ketyl is nonplanar, with an out-of-plane angle of 24–27° and close to that of the excited (n-π^*) neutral molecule. The nitrogen and carbon-13 splittings are positive and increase with the out-of-plane torsion at the radical site.

Nitroxides are one of the most remarkable series of free radicals,[2a] the interest of which has grown in recent years as a consequence of their extensive use for biological studies. Esr measurements in spin-label experiments[2b] are generally interpreted on the assumption of a planar radical site in spite of the fact that the nitroxide group is known to exist in both planar[3] ($\alpha = 0°$) and bent[4] ($\alpha \neq 0°$) geometries. On the other hand, the question of the geometry around the radical carbon in the isoelectronic ketyl series has recently been the object of both experimental[5] and theoretical[6] in-