

Expansion of Molecular Orbital Wave Functions into Valence Bond Wave Functions. A Simplified Procedure

P. C. Hiberty* and C. Leforestier

Contribution from the Laboratoire de Chimie Théorique¹ (490), Université de Paris-Sud, 91405 Orsay, France. Received June 23, 1977

Abstract: A method is proposed to expand molecular orbital wave functions into valence bond wave functions, and to calculate rigorously the weights of the corresponding structures in a given electronic state, avoiding the storage of the overlap terms between valence bond functions. Application to BH₃, CH₃, NH₃, OH₃⁺, and a series of 17 1,3-dipoles is presented. All allyl-like 1,3-dipoles are found to have a strong diradical character. The effects of configuration interaction are compared. The results are in agreement with the available calculations by the generalized valence bond method.

I. Introduction

The comparison between Hartree-Fock and Heitler-London methods is an old subject of interest. The example of the H₂ molecule is well known, and has been discussed by Slater² and Mulliken.³ Several authors have projected valence bond (VB) functions onto molecular orbital (MO) ones in the case of small systems,⁴⁻⁶ involving three or four atomic orbitals; larger systems have also been treated^{7,8} but then only a few VB functions were projected. In all cases, the aim is to evaluate the weights of various bond structures, represented by the VB functions, in the total MO wave functions. To avoid the difficulty of the nonorthogonality of the VB functions, the weight of a structure is generally expressed as the square of the projection of the corresponding VB function onto the MO function. Nevertheless, a rigorous definition has been proposed⁹⁻¹¹ (see next section), and used in some calculations.^{6b}

Here we present a relatively simple method which projects any minimal basis set LCAO-MO wave function onto a *complete* basis of VB functions, and which evaluates rigorously the weights of the corresponding structures in a given electronic state. The computer program associated with this method is written in PL/1 language, and is restricted to singlet states in its preliminary version.

II. Method

The method is applied to Hartree-Fock type antisymmetrized wave functions ψ_{HF} which are linear combinations of Slater determinants:

$$|\psi_1 \bar{\psi}_1 \dots \bar{\psi}_i \psi_j \dots| \quad (1)$$

where the ψ_i 's are molecular orbitals expressed as linear combinations of atomic orbitals (LCAO) ϕ_μ

$$\psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}$$

The basic principle is to expand each Slater determinant into a linear combination of determinants involving only atomic orbitals (AO determinants). Then these AO determinants are regrouped to form classical valence-bond functions of the form

$$V_m = \sum_{\text{all bonds}} (-1)^I I |\phi_1 \bar{\phi}_2 \phi_3 \bar{\phi}_4 \dots \phi_{\mu} \bar{\phi}_{\nu} \dots| \quad (2)$$

where I is a spin inversion between two bonded atomic orbitals. One can prove easily that any antisymmetrized LCAO-MO wave function can be expanded in such a manner without any residual term.¹²

The main difficulty comes from the overcompleteness of the basis formed by all possible valence-bond functions built on a given set of atomic orbitals. Projection of a MO wave func-

tion onto such a basis would give an infinite number of solutions. This difficulty can be overcome by a classical method, due to Rumer,¹³ which generates a linearly independent set of VB functions. The atomic orbitals are arranged on a circle and connected by segments. Then the schemes represented by noncrossing segments are selected and the VB functions corresponding to these bonding schemes form an independent and complete set. We put into shape a PL/1 program using the Rumer method to generate the VB functions. For entirely covalent structures, all AOs are arranged on the circle, while, for the polar structures, Rumer's circle is restricted to the noncharged AOs. After this has been done for all possible schemes, the VB functions V_m are normalized to unity. If we now express a MO configuration (C_{MO}) as a linear combination of VB functions

$$C_{\text{MO}}^k = \sum_m J_m^k V_m \quad (3)$$

and if we expand the V_m 's into AO determinants, we can identify this expression with the previous expansion of Slater determinants in terms of eq 2. One obtains M equations with M unknowns, where M is the total number of *linearly independent* structures describing the calculated molecule. This system can be reduced to many subsystems, each of them involving only the determinants corresponding to the same overall charge distribution in the AOs. If ψ_{HF} is a linear combination of MO configuration

$$\psi_{\text{HF}} = \sum_k d_k C_{\text{MO}}^k \quad (4)$$

the above system of equations is solved for each C_{MO}^k , and one can obtain ψ_{HF} in terms of VB functions by combining eq 3 and 4:

$$\psi_{\text{HF}} = \sum_m K_m V_m$$

To calculate the weight (W_m) of a given VB structure in the state described by ψ_{HF} , several definitions may be used. The simplest way is to take the square of the projection of V_m onto ψ_{HF} , namely K_m^2 . This definition, commonly used,^{4,7a,8} suffers from a lack of coherence.¹⁴ A much more rigorous one⁹⁻¹¹ consists of adding to K_m^2 half of the overlap terms between V_n and the other V_n 's involved in $|\psi_{\text{HF}}|^2$. The weight W_m of a classical valence bond structure is then given by

$$W_m = K_m^2 + \sum_{n \neq m} K_m K_n \langle V_m | V_n \rangle \quad (5)$$

Significant discrepancies between the results given by both definitions may exist when the AOs of the calculated molecule overlap strongly; here we choose the most rigorous formula (eq 5) to calculate the weights.

The procedure outlined above may be applied straightforwardly for very small molecules, such as the π MOs of allyl ions, butadiene, etc. However, it necessitates the storage of all the coefficients of the AO determinants in ψ_{HF} , and especially of all the overlap terms between the VB functions. The number of such terms becomes tremendous for moderate-sized molecules. For example, the π MO system of naphthalene involves 63 504 AO determinants, 19 404 independent VB functions, and about 2×10^9 overlap terms. To overcome this difficulty, we propose a procedure to expand the MO determinants (D_{MO}) which strongly reduces the main storage requirements without losing the accuracy of the above definition (eq 5). Let us first evaluate the coefficient of a given AO determinant after regrouping all equivalent ones, i.e., all determinants including the same atomic spin orbitals. For the sake of clarity, α spin orbitals are gathered on the left-hand side, and β spin orbitals on the right-hand side, so that

$$D_{\text{MO}} = |\psi_1 \dots \psi_i \dots \psi_N \bar{\psi}_1 \dots \bar{\psi}_j \dots \bar{\psi}_N| \quad (6)$$

We call $d(r, r')$ the AO determinant $|\dots \phi_\mu \phi_\nu \dots \bar{\phi}_{\mu'} \bar{\phi}_{\nu'} \dots|$, where the ϕ_μ 's are arranged by increasing indices; r and r' are characteristic of a certain distribution of spins α and β , respectively, among the AOs. If we do not regroup the determinants equivalent by column permutations, the coefficient of $d(r, r')$ in D_{MO} is

$$A(r, r') = (\dots C_{\mu i} C_{\nu j} \dots C_{\mu' i'} \dots C_{\nu' j'} \dots)$$

The equivalent AO determinant deduced from the first one by permuting two atomic orbitals ϕ_μ and ϕ_ν has as coefficient the product

$$- (\dots C_{\nu i} \dots C_{\mu j} \dots C_{\mu' i'} \dots C_{\nu' j'} \dots)$$

If one generalizes to all permutations between orbitals of the same spin, and denotes as $B(r, r')$ the sum of the coefficients of all determinants equivalent to $d(r, r')$, one obtains

$$B(r, r') = \sum_P (-1)^P P[\dots C_{\mu i} C_{\nu j} \dots] \times \sum_P (-1)^P P[\dots C_{\mu' i'} C_{\nu' j'} \dots] \quad (7)$$

where P is a permutation between the first indices of the $C_{\mu i}$ or $C_{\mu' i'}$ terms.

A similar factorization can be made in the calculation of the overlap between two AO determinants $d(r, r')$ and $d(s, s')$:

$$\begin{aligned} \langle d(r, r') | d(s, s') \rangle &= \langle \mathcal{A}(\dots \phi_\mu \phi_\nu \dots \bar{\phi}_{\mu'} \bar{\phi}_{\nu'} \dots) | \mathcal{A}(\dots \phi_\lambda \phi_\sigma \dots \bar{\phi}_{\lambda'} \bar{\phi}_{\sigma'} \dots) \rangle \\ &= \frac{1}{N!} \sum_{P'} (-1)^{P'} P' \left(\sum_{P''} (-1)^{P''} P'' \right. \\ &\quad \left. \times (\dots S_{\mu\lambda} \dots S_{\nu\sigma} \dots S_{\mu'\lambda'} S_{\nu'\sigma'} \dots) \right) \quad (8) \end{aligned}$$

where \mathcal{A} is the usual antisymmetrizing operator, N is the total number of electrons, P' permutes the first indices of the S terms, P'' permutes the second indices, and the S terms are overlaps between two atomic orbitals:

$$S_{\mu\lambda} = \langle \phi_\mu | \phi_\lambda \rangle$$

As the effects of operators P' and P'' are redundant, one can simplify eq 8, which becomes

$$\langle d(r, r') | d(s, s') \rangle = \sum_{P'} (-1)^{P'} P'(\dots S_{\mu\lambda} S_{\nu\sigma} \dots S_{\mu'\lambda'} S_{\nu'\sigma'} \dots) \quad (9)$$

Remembering that the overlaps between orbitals of different spins are zero, one can write

$$\begin{aligned} \langle d(r, r') | d(s, s') \rangle &= \sum_{P'} (-1)^{P'} P'(\dots S_{\mu\lambda} S_{\nu\sigma} \dots) \\ &\quad \times \sum_{P'} (-1)^{P'} P'(\dots S_{\mu'\lambda'} S_{\nu'\sigma'} \dots) \quad (10) \end{aligned}$$

where the indices μ, ν and μ', ν' refer respectively to α and β atomic spin orbitals of the AO determinant $d(r, r')$, while the indices λ, σ and λ', σ' refer to that of the AO determinant $d(s, s')$.

Let us now define, for any AO determinant $d(r, r')$, a couple of two "half-determinants" $h_{(r)}^\alpha$ and $h_{(r')}^\beta$, involving respectively the α and β atomic spin orbitals of $d(r, r')$:

$$d(r, r') = (h_{(r)}^\alpha, h_{(r')}^\beta)$$

The "half-determinants" $h_{(r)}^\alpha$ and $h_{(r')}^\beta$ have no physical meaning, but are characteristic of a certain spin distribution among the AOs. One can define similarly $h_{(\text{MO})}^\alpha$ and $h_{(\text{MO})}^\beta$ by the following expression:

$$D_{\text{MO}} = (h_{(\text{MO})}^\alpha, h_{(\text{MO})}^\beta) \quad (11)$$

where $h_{(\text{MO})}^\alpha$ and $h_{(\text{MO})}^\beta$ now involve respectively α and β molecular spin orbitals. Now instead of expanding MO determinants into AO determinants, as in the straightforward procedure, we expand MO half-determinants into AO half-determinants:

$$h_{(\text{MO})}^\alpha = \sum_{\text{all } r} C_r^\alpha h_{(r)}^\alpha$$

$$h_{(\text{MO})}^\beta = \sum_{\text{all } r'} C_{r'}^\beta h_{(r')}^\beta$$

The expansion coefficients C_r^α and $C_{r'}^\beta$ are precisely the quantities whose product gives $B_{(r, r')}$ in eq 7:

$$C_r^\alpha = \sum_P (-1)^P P[\dots C_{\mu i} C_{\nu j} \dots]$$

$$C_{r'}^\beta = \sum_{P'} (-1)^{P'} P'[\dots C_{\mu' i'} C_{\nu' j'} \dots]$$

the indices μ, ν and μ', ν' referring respectively to the α and β atomic spin orbitals involved in the spin distributions r and r' .

In the same way, one can define an overlap between two half-determinants of the same spin, $h_{(r)}^\alpha$ and $h_{(s)}^\alpha$, as

$$S_{rs} = \sum_{P'} (-1)^{P'} P'(\dots S_{\mu\lambda} S_{\nu\sigma} \dots) \quad (12)$$

where the μ, ν and λ, σ indices refer to α spin orbitals involved in the half-determinants $h_{(r)}^\alpha$ and $h_{(s)}^\alpha$. Then the coefficient of a given determinant $d(r, r')$ in D_{MO} is expressed as

$$B_{(r, r')} = C_r^\alpha C_{r'}^\beta \quad (13)$$

and, inserting eq 12 into eq 10, the overlap between two AO determinants becomes

$$\langle d(r, r') | d(s, s') \rangle = S_{rs} S_{r's'} \quad (14)$$

The advantage of this procedure is that all operations such as normalization of a VB function, evaluation of its projection onto ψ_{HF} , and evaluation of the weight of the corresponding structure can be made by using formulas 13 and 14, and one only need store the terms K_m , C_r^α , $C_{r'}^\beta$, S_{rs} , and $S_{r's'}$. For example, expansion of the π MO system of naphthalene, by our procedure, only needs the storage of about 3×10^4 S_{rs} terms instead of 2×10^9 with the straightforward procedure. On the other hand, this procedure strongly reduces the computing time since expansion of half-determinants is much more rapid than expansion of complete determinants.

Table I. Main Structural Weights¹⁷ of BH₃, CH₃, Planar NH₃, and H₃O⁺.

	Boron hydride A = B	Methyl radical A = C·	D _{3h} ammonia A = N	Solvated proton A = O ⁺	No. of equivalent structures
	0.127	0.133	0.135	0.086	1
	0.072	0.058	0.044	0.015	3
	0.055	0.072	0.088	0.097	3
	0.040	0.025	0.014	0.002	3
	0.024	0.039	0.060	0.111	3
	0.031	0.032	0.031	0.019	6
	0.023	0.011	0.004	0.0	1
	0.010	0.021	0.039	0.127	1
	0.014	0.018	0.022	0.024	3
	0.018	0.014	0.011	0.004	3

III. Additional Problems

1. Choice of Hybridization. In order to have proper valence bond functions, the atomic orbitals must be expressed as hybrid orbitals in the case of σ bonds. For molecules having the classical bond angles 109.5, 120, and 180°, the choice of hybridization is obvious. For different molecules, one could wonder whether or not it is important to build accurate hybrid orbitals, reproducing whenever possible the real bond angles. To test this point, we used an unadapted basis of hybrid orbitals for the correct D_{3h} geometry of the methyl radical. This basis consists of a sp hybrid, pointing toward a hydrogen atom, and of two sp^3 hybrids pointing between the two remaining hydrogens and forming a 109.5° angle. The calculated weights are not very different from those calculated with the correct hybridization, the discrepancy being of the order of 4% for the largest weights and 10% for the smallest ones. This suggests that, in most of the cases, the classical sp , sp^2 , and sp^3 hybrids may be used to form the AO basis set. Unless otherwise specified, these were indeed the hybrids chosen for the VB structures.

2. Expansion into Mixed Determinants. In most of the cases, there are clearly certain orbitals which have the same occupancy in all the VB structures, for example, those involved in the inner shell. Generalizing, one may be interested only with certain bonds, particularly subject to delocalization, of a given molecule, and wish to "freeze" the remaining bonds, thus dealing only with a restricted set of VB structures. A complete

Table II. Optimized Bond Lengths (Å) Connecting the Heavy Atoms of Some 1,3-Dipoles^a

Ozone	O — 1.317 — O — 1.317 — O
Nitroso oxides	∖N — 1.330 — O — 1.286 — O
Nitrosimines	∖N — 1.325 — O — 1.325 — N∕
Carbonyl oxides	>C — 1.367 — O — 1.269 — O
Carbonyl imines	>C — 1.333 — O — 1.306 — N∕
Carbonyl ylides	>C — 1.342 — O — 1.342 — C<
Nitro compounds	O — 1.296 — N — 1.296 — O
Azoxy compounds	∖N — 1.342 — N — 1.290 — O
Azimes	∖N — 1.340 — N — 1.340 — N∕
Nitrones	>C — 1.345 — N — 1.276 — O
Azomethine imines	>C — 1.368 — N — 1.293 — N∕
Azomethine ylides	>C — 1.370 — N — 1.370 — C<
Nitrous oxide	O — 1.264 — N — 1.159 — N
Azides	∖N — 1.279 — N — 1.169 — N
Diazoalkanes	>C — 1.308 — N — 1.191 — N
Nitrile imines	∖N — 1.289 — N — 1.178 — C-
Nitrile ylides	>C — 1.309 — N — 1.188 — C-

^aIn our calculations, all substituents are hydrogens.

expansion into determinants involving only atomic orbitals would lead to a much too large number of VB structures, and the results concerning the interesting part of the molecule would be scattered in an excess of information. An alternative is to expand ψ_{HF} into mixed determinants. Let us call "invariant set" the MOs corresponding to the frozen bonds, the inner shell, and all orbitals whose occupancy is assumed to be the same in the restricted set of VB structures. The "variant" set is composed of the other MOs. If the two sets do not mix, one can define mixed determinants as being built with MOs from the invariant set and AOs from the variant one. This nonmixing condition is satisfied by symmetry in certain cases, such as conjugated molecules where the variant set is restricted to the π orbitals. For more general cases, it is necessary to use a localization procedure to separate both sets of MOs.

IV. Applications

1. AH₃ Molecules: BH₃, CH₃, Planar NH₃, OH₃⁺. Boron hydride is known to be planar, with D_{3h} symmetry. We optimized its bond lengths (B-H = 1.139 Å), with a minimal basis set STO-3G ab initio program;¹⁵ examination of molecular orbitals of this molecule shows that the 1s orbital of B is practically not mixed with the 2s one. Hence, assuming that

Table III. Structural Weights of the Ground States of 1,3-Dipoles, Calculated after 6×6 CI^a

$O=O^+=O$ 0.184 (0.226)	$O=O^+-O^-$ 0.184 (0.226)	$\dot{O}-O-\dot{O}$ 0.593 (0.213)	O^+-O-O^- 0.008 (0.107)	O^-O-O^+ 0.008 (0.107)	$O^{\pm}O^{\pm}O^-$ 0.023 (0.120)
$>C=O^+=O$ 0.059 (0.145)	$>C=O^+-O^-$ 0.326 (0.288)	$>\dot{C}-O-\dot{O}$ 0.434 (0.208)	$>C^+-O-O^-$ 0.105 (0.207)	$>C=O-O^+$ 0.005 (0.052)	$>C^{\pm}O^{\pm}O^-$ 0.071 (0.100)
$\backslash N=O^+=O$ 0.134 (0.175)	$\backslash N=O^+-O^-$ 0.264 (0.268)	$\backslash \dot{N}-O-\dot{O}$ 0.551 (0.214)	$\backslash N^+-O-O^-$ 0.021 (0.164)	$\backslash N=O-O^+$ 0.005 (0.070)	$\backslash N^{\pm}O^{\pm}O^-$ 0.025 (0.110)
$\backslash N=O^+=N^-$ 0.182 (0.217)	$\backslash N=O^+-N^-$ 0.182 (0.217)	$\backslash \dot{N}-O-\dot{N}^-$ 0.538 (0.233)	$\backslash N^+-O-N^-$ 0.008 (0.116)	$\backslash N=O-N^+$ 0.008 (0.116)	$\backslash N^{\pm}O^{\pm}N^-$ 0.080 (0.101)
$>C=O^+=N^-$ 0.144 (0.171)	$>C=O^+-N^-$ 0.264 (0.259)	$>\dot{C}-O-\dot{N}^-$ 0.531 (0.226)	$>C^+-O-N^-$ 0.027 (0.171)	$>C=O-N^+$ 0.007 (0.075)	$>C^{\pm}O^{\pm}N^-$ 0.026 (0.098)
$>C=O^+=C<$ 0.197 (0.213)	$>C=O^+-C<$ 0.197 (0.213)	$>\dot{C}-O-\dot{C}<$ 0.552 (0.240)	$>C^+-O-C<$ 0.015 (0.120)	$>C=O-C^+<$ 0.015 (0.120)	$>C^{\pm}O^{\pm}C<$ 0.025 (0.094)
$O=N^+=O$ 0.205 (0.234)	$O=N^+-O^-$ 0.205 (0.234)	$\dot{O}-N-\dot{O}$ 0.527 (0.196)	O^+-N-O^- 0.012 (0.098)	$O=N-O^+$ 0.012 (0.098)	$O^{\pm}N^{\pm}O^-$ 0.038 (0.140)
$\backslash N=N^+=O$ 0.167 (0.200)	$\backslash N=N^+-O^-$ 0.247 (0.259)	$\backslash \dot{N}-N-\dot{O}$ 0.523 (0.204)	$\backslash N^+-N-O^-$ 0.019 (0.132)	$\backslash N=N-O^+$ 0.009 (0.079)	$\backslash N^{\pm}N^{\pm}O^-$ 0.036 (0.127)
$\backslash N=N^+=N^-$ 0.200 (0.225)	$\backslash N=N^+-N^-$ 0.200 (0.225)	$\backslash \dot{N}-N-\dot{N}^-$ 0.540 (0.218)	$\backslash N^+-N-N^-$ 0.014 (0.109)	$\backslash N=N-N^+$ 0.014 (0.109)	$\backslash N^{\pm}N^{\pm}N^-$ 0.032 (0.116)
$>C=N^+=O$ 0.148 (0.166)	$>C=N^+-O^-$ 0.268 (0.287)	$>\dot{C}-N-\dot{O}$ 0.444 (0.198)	$>C^+-N-O^-$ 0.034 (0.171)	$>C=N-O^+$ 0.004 (0.057)	$>C^{\pm}N^{\pm}O^-$ 0.104 (0.121)
$>C=N^+=N^-$ 0.168 (0.198)	$>C=N^+-N^-$ 0.253 (0.247)	$>\dot{C}-N-\dot{N}^-$ 0.509 (0.219)	$>C^+-N-N^-$ 0.024 (0.137)	$>C=N-N^+$ 0.012 (0.088)	$>C^{\pm}N^{\pm}N^-$ 0.034 (0.112)
$>C=N^+=C<$ 0.209 (0.221)	$>C=N^+-C<$ 0.209 (0.221)	$>\dot{C}-N-\dot{C}<$ 0.514 (0.224)	$>C^+-N-C<$ 0.017 (0.112)	$>C=N-C^+<$ 0.017 (0.112)	$>C^{\pm}N^{\pm}C<$ 0.033 (0.109)
$O=N^+=N$ 0.378 (0.372)	$O=N^+=N^-$ 0.191 (0.112)	$\dot{O}-N=N$ 0.167 (0.124)	$O^+-N=N^-$ 0.0 (0.019)	$O=N=N^+$ 0.130 (0.205)	$O^{\pm}N^{\pm}N^-$ 0.135 (0.169)
$\backslash N=N^+=N$ 0.293 (0.270)	$\backslash N=N^+=N^-$ 0.252 (0.220)	$\backslash \dot{N}-N=N$ 0.316 (0.162)	$\backslash N^+-N=N^-$ 0.015 (0.066)	$\backslash N=N=N^+$ 0.029 (0.100)	$\backslash N^{\pm}N^{\pm}N^-$ 0.093 (0.184)
$>C=N^+=N$ 0.164 (0.184)	$>C=N^+=N^-$ 0.414 (0.305)	$>\dot{C}-N=N$ 0.281 (0.154)	$>C^+-N=N^-$ 0.042 (0.128)	$>C=N=N^+$ 0.010 (0.047)	$>C^{\pm}N^{\pm}N^-$ 0.089 (0.182)
$\backslash N=N^+=C-$ 0.372 (0.312)	$\backslash N=N^+=C-$ 0.189 (0.174)	$\backslash \dot{N}-N=C-$ 0.287 (0.157)	$\backslash N^+-N=C-$ 0.009 (0.044)	$\backslash N=N=C^+$ 0.052 (0.141)	$\backslash N^{\pm}N^{\pm}C-$ 0.090 (0.173)
$>C=N^+=C-$ 0.247 (0.239)	$>C=N^+=C-$ 0.316 (0.249)	$>\dot{C}-N=C-$ 0.297 (0.167)	$>C^+-N=C-$ 0.025 (0.087)	$>C=N=C^+$ 0.023 (0.080)	$>C^{\pm}N^{\pm}C-$ 0.092 (0.178)

^a The weights of the ground configurations are indicated in parentheses.

in all structure the 1s orbital of B is doubly occupied, one can restrict the variant set of MOs to the six bonding and anti-bonding MOs of the valence shell. A simple canceling of the 1s terms into the variant set would affect the normality of the MOs. Hence, to maintain the normality, the coefficient of the 2s AO in the lowest B-H bonding MO and the highest anti-bonding MO is slightly corrected (by a factor of 0.96, approximately). The basis of atomic orbitals generating the variant set is composed of the three 1s orbitals of hydrogens and the three sp^2 hybrids of boron.

Similarly, for the methyl radical and the solvated proton, we excluded the inner shell from the variant set of MOs. In addition we included in the invariant set the p orbital perpendicular to the molecular plane, which is occupied in these molecules, but does mix with the other orbitals for symmetry reasons and consequently keeps the same occupancy for all structures. This simplification still holds for the ammonia

molecule if it is taken in its planar form. As for boron hydride, the three molecules CH_3 , NH_3 , and OH_3^+ have the D_{3h} symmetry and optimized bond lengths¹⁶ ($C-H = 1.078 \text{ \AA}$, $O^+-H = 0.983 \text{ \AA}$, $N-H = 1.006 \text{ \AA}$).

For these AH_3 -type molecules, only single-determinantal wave functions, representing the ground configuration, have been expanded. Among the 175 structures of each AH_3 molecule, only ten of them have been selected as being the most representative. The weights of these leading structures are displayed in Table I. All other ones, as for example those involving a hydrogen 1s orbital and the hybrid pointing toward it bearing the same charge, have a weight smaller than 10^{-3} . The calculated weights are in accordance with the electronegativity scale since electron-rich structures of the central atom are more and more important from boron to oxygen, but the weights of the entirely covalent structures are surprisingly low. This reflects the general tendency of single-determinant

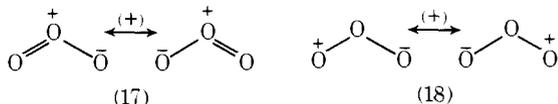
Hartree-Fock methods to overestimate the weight of the ionic structures, and would certainly be corrected by an extensive configuration interaction. Nevertheless, even at the SCF stage, one can notice the particular structure of the solvated proton, whose best representation is the sum of three resonance formulas of the type $\text{HO}^- + 2\text{H}^+$ (weight = $3 \times 0.111 = 0.333$). This suggests that the usual representation of the solvated proton, a dative bond from H_2O to H^+ , is wrong. Indeed, such a structure is intermediate between the symmetrized structure (15) and the structure (16), which come only in second and



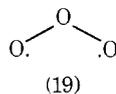
fifth position, respectively. One can also notice the strikingly important weight (0.127) of the oxygen dianion surrounded by three protons.

2. Ozone and Other 1,3-Dipoles. We decomposed the wave functions of the ground configuration and of the ground state (obtained after a 6×6 CI calculation over all π orbitals) for a series of 1,3-dipoles. For these conjugated molecules, we took as invariant set all the orbitals composing the σ skeleton. So the variant set is restricted to the π orbitals perpendicular to the molecular plane. We chose standard bond angles, i.e., 120° between sp^2 hybrids and 180° between sp ones. We optimized, after CI, the bond lengths connecting the heavy atoms¹⁸ (see Table II). All substituents are hydrogens, and the following standard parameters have been used: $\text{N-H} = 1.01 \text{ \AA}$, $\text{C}_{\text{sp}^2}\text{-H} = 1.08 \text{ \AA}$, $\text{C}_{\text{sp}}\text{-H} = 1.06 \text{ \AA}$.

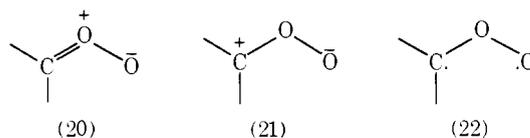
The results of the expansion calculation for these 1,3-dipoles are displayed in Table III. It is interesting to compare the structural weights corresponding to the ground states (obtained after CI) to those corresponding to the ground configurations, for it emphasizes the effect and importance of CI. For example, the ozone molecule is usually represented in its two zwitterionic forms (17) and (18): (17) and (18) are symmetrized structures,



and their weights can be calculated as twice the weight of $\text{O}=\text{O}^+-\text{O}^-$ and $\text{O}^+-\text{O}-\text{O}^-$, respectively. Table III shows that (17) and (18) are a good description of the ground configuration of ozone, since their respective weights are 0.452 and 0.214, respectively, in this configuration. But the ground state after 6×6 CI is strikingly different, since now the diradical structure (19) becomes the leading structure, with a weight



of 0.593, against 0.368 for (17). Furthermore, the unlikely structure involving a dication as central atom disappears almost completely, as also, surprisingly, the often written structure (18). These results are in accordance with a sophisticated generalized valence bond calculation by Goddard,²⁰ which indicates that ozone is best described as a diradical, and that (18) is not involved in the low-lying states. Another 1,3-dipole, carbonyl oxide, involved in the ozonolysis mechanism, is usually called the Criegee zwitterion, and represented by (20) and (21). Goddard's²¹ calculations and our results again support the diradical structure (22), since our calculated structural weights are 0.434 for (22) vs. 0.326 for (20) and 0.105 for (21). Again the dipolar structure (21), commonly accepted, is found very unlikely by Goddard²¹ and by our



calculations. The diradical structure (22) is in accordance with a number of experimental data; it has been suggested by Murray²² and Hamilton and Giacini,²³ who obtained the Criegee intermediate by photolysis of diazo compounds. On the other hand, the diradical character explains the very weak barrier to rotation²⁴ around the CO bond. This diradical character is common to all the allyl-like 1,3-dipoles that we calculated (ozone to azomethine ylides). On the contrary, the zwitterionic structures are much more important, and become the leading structures, in the case of propargyl-allyl-like dipoles (nitrile ylides to nitrous oxide). Here there is a discrepancy between our results and those of Goddard,²⁶ whose GVB calculations describe the ground state of diazomethane as a diradical (23). Our calculations rather support the zwitterionic structure (24), since the corresponding calculated



weight is 0.414 vs. 0.281 for (23). Yet our results seem to be in agreement with the experimental CN bond length of 1.30 Å, which is typically that of a CN double bond.

V. Concluding Remarks

The method described above can be used as a tool for interpreting the information given in a molecular orbital wave function, as well as for comparing Hartree-Fock methods with valence bond methods. With moderate-sized CI, it is expected that Hartree-Fock methods favor the ionic structures, while valence bond methods favor the covalent or diradical ones. This is probably the nature of the discrepancy between both types of calculations in the case of diazomethane. On the contrary, the agreement looks good for the allyl-like 1,3-dipoles and should lead to firm chemical predictions. In particular, the importance of the spin-paired diradical structure now appears as well established for this last type of molecule, in accordance with Harcourt's suggestions.^{7d,27} Application of a localization procedure should allow us to describe medium-sized molecules with a reasonable amount of structures, and to visualize excited intermediates involved in photochemistry and transition states of organic reactions. This, together with the extension of the program to higher multiplicities, will be undertaken in the near future.

Acknowledgments. Professor Lionel Salem is gratefully acknowledged for his constant encouragement and pertinent advice. The authors are also indebted to Professors J. P. Malrieu, G. Berthier, and J. P. Daudey for helpful discussions.

References and Notes

- (1) The Laboratoire de Chimie Théorique is associated with the CNRS (ERA no. 549).
- (2) J. C. Slater, *J. Chem. Phys.*, **43**, S11 (1965), and references cited therein.
- (3) R. S. Mulliken, *Phys. Rev.*, **41**, 49 (1932).
- (4) R. S. Berry, *J. Chem. Phys.*, **30**, 936 (1959).
- (5) R. D. Harcourt and A. Harcourt, *J. Chem. Soc., Faraday Trans. 2*, **70**, 743 (1974).
- (6) (a) W. A. Kirchoff, J. Farren, and J. W. Linnett, *J. Chem. Phys.*, **42**, 1410 (1965); (b) D. M. Hirst, and J. W. Linnett, *ibid.*, **43**, S74 (1965); (c) *J. Chem. Soc.*, 1035, 3844 (1962).
- (7) (a) R. D. Harcourt, *Theor. Chim. Acta*, **2**, 437 (1964); (b) *ibid.*, **6**, 131 (1966); (c) *Int. J. Quantum Chem.*, **4**, 173 (1970); (d) R. D. Harcourt and J. F. Sillitoe, *Aust. J. Chem.*, **27**, 691 (1974).
- (8) M. Craig and R. S. Berry, *J. Am. Chem. Soc.*, **89**, 2801 (1967).

- (9) S. Takekiyo, *Bull. Chem. Soc. Jpn.*, **34**, 1466 (1961).
 (10) (a) A. C. Hurley, *J. Chem. Phys.*, **26**, 376 (1957); (b) *Proc. R. Soc. London, Ser. A*, **248**, 119 (1958).
 (11) D. Peters, *J. Am. Chem. Soc.*, **84**, 3812 (1962).
 (12) Indeed both ψ_{HF} and the VB functions are spin eigenfunctions of the electronic state. If ψ_{HF} could be expanded into a set of VB functions plus residual terms, it would be no longer a spin eigenfunction.
 (13) G. Rumer, *Goettingen Nachr.*, 377 (1932).
 (14) Indeed, if the valence bond functions are properly normalized, this definition implies that the weight of a symmetrized structure, $V_m \pm V_n$, is not equal to the sum of the weights of V_m and V_n . As a consequence, the weight of the covalent structure of H_2 , for example, would depend on the way the MO function is expanded, i.e., into symmetrized ($H^+H^- \pm H^-H^+$) or non-symmetrized (H^+H^- and H^-H^+) VB functions. This inconvenience disappears with the rigorous definition.
 (15) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1970); (b) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, QCPE No. 236, Indiana University, Bloomington, Ind.
 (16) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971).
 (17) For some molecules, the main weights add to a number slightly greater

- than unity. This is due to the fact that, for very unlikely structures, the term K_m^2 is smaller than the overlap term $\sum_{n \neq m} K_m K_n (V_m | V_n)$, and consequently some W_m terms may be negative. In our examples, no negative weight has an absolute value greater than 5×10^{-3} .
 (18) The geometries of nitrile imine and nitrile ylide have already been fully optimized,¹⁹ in STO-3G basis set, at the SCF stage. Owing to the inclusion of Cl, our optimized bond lengths are slightly different.
 (19) P. Caramella and K. N. Houk, *J. Am. Chem. Soc.*, **98**, 6397 (1976).
 (20) (a) T. H. Dunning, Jr., and W. A. Goddard III, *J. Chem. Phys.*, **62**, 3912 (1975); (b) W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973).
 (21) W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 3004 (1975).
 (22) R. W. Murray and A. Suzul, *J. Am. Chem. Soc.*, **95**, 3343 (1973).
 (23) G. A. Hamilton and J. R. Glacin, *J. Am. Chem. Soc.*, **88**, 1584 (1966).
 (24) This barrier, calculated in the 4-31G basis set,²⁵ is 12.4 kcal/mol. A π POL(2)-Cl calculation by Wadt and Goddard²¹ evaluates it as 17.5 kcal/mol. In both cases, this rotational barrier is sufficiently weak to allow a fast isomerization at room temperature.
 (25) P. C. Hiberty, *J. Am. Chem. Soc.*, **98**, 6088 (1976).
 (26) S. P. Walch and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 5319 (1975).
 (27) R. D. Harcourt, *J. Mol. Struct.*, **12**, 351 (1974).

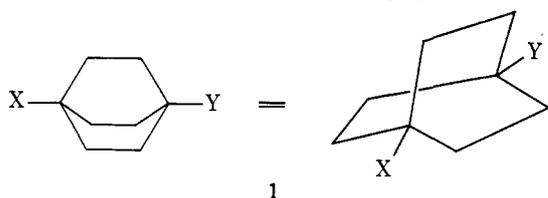
Molecular Orbital Studies of Organic Substituent Effects. Transmission of Charge and Energy Perturbations through Rigid Bicyclic Skeletons in a Model S_N2 Reaction

Robert B. Davidson* and C. Richard Williams

Contribution from the Chemistry Department, Amherst College, Amherst, Massachusetts 01002. Received June 22, 1977

Abstract: Substituent effects on model S_N2 exchange reactions of 4-substituted bicyclo[2.2.2]octylcarbinyl and cubylcarbinyl chlorides are examined in a series of CNDO/2 semiempirical molecular orbital calculations. The energetic trends produced by substitution in the two sets of aliphatic compounds are correlated with each other and with related experimental data; substituent effects in the two series were quite comparable. Interaction of substituents with the (charged) model transition state reaction site dominated a much smaller interaction with the (neutral) carbinyl chloride group. In all cases, the electron distribution in a carbinyl chloride and its corresponding model transition state were almost identically affected by a given substituent. An inductive pattern of charge perturbation (of uncertain energetic importance) was observed.

Rigid bicyclic molecules, especially those with the 4-bicyclo[2.2.2]octyl (BCO) skeleton (1), have played a central role

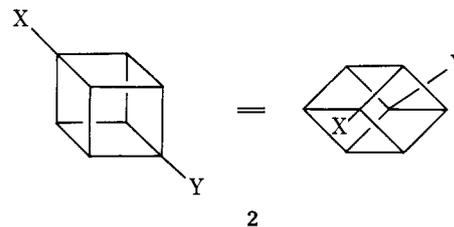


in experimental studies which attempt to separate the effects of substitution into components which differ in their origin and mode of transmission. Because these bicyclic compounds lack the aromatic π electron systems of benzene derivatives (in which substituent effects have been most thoroughly studied) but share the latter's rigidity, their properties have been used to assess the special transmission characteristics of those π systems.¹

The experimental studies do not allow an unambiguous evaluation of the relative importance of "inductive" and "resonance" contributions to observed substituent effects.² For one thing, *inductive* distortions of benzene π electrons seem to contribute significantly to observed substituent effects in at least some aromatic systems³ (though such distortions were not very important in a study of benzyl chloride S_N2 reactions analogous to this one⁴). For another, it has been suggested that *conjugative* transmission mechanisms may operate in the bicyclic saturated compounds. Analogous through-bond cou-

pling⁵ operates in similar systems and the BCO molecule (see Figure 1) has valence orbitals of symmetry appropriate to the coupling of either π or σ orbitals of substituent and reaction site.⁶ It has been argued⁷ that such coupling is not required to explain the available data but this question has not been thoroughly explored.

In another attempt to distinguish different modes of transmission, Stock⁷ has compared substituent effects in BCO derivatives with those in similar compounds in which the BCO framework has been replaced by the 4-cubyl skeleton (2). He



argued that because the spatial relationship of substituent to reaction site is quite similar in the two series, through-space electrostatic field effects⁸ should be similar, and that if this were the dominant mechanism of transmission measured substituent effects ought also to be rather comparable. If, on the other hand, the classical inductive effect (wherein successively polarized bonds carry the substituent's electrical disturbance to the reaction site⁹) were dominant, the cubane compounds ought to exhibit larger effects because there are