

Appendix

In this work, we have used CNDO/2 and INDO SCF-MO calculations in order to illustrate qualitatively several theoretical points. The computations were carried out on a CDC-6400 computer utilizing a computer program which is essentially identical with the one of Pople and Dobosh described in ref 29. In all

cases, standard bond lengths and bond angles were used. In one case, the π MO's of the FHC- fragment were determined by a simple Hückel MO calculation with the following input parameters: $H_{FF} = \alpha + 2.1\beta$, $H_{CC} = \alpha$, $H_{CF} = 1.25\beta$, $\alpha = 0$, $\beta = -2.88$ eV.

(29) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

Semiempirical MC-SCF Theory. I. Closed Shell Ground State Molecules

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Abstract: A new semiempirical molecular orbital theory, based on the zero differential overlap approximation, is presented. In this theory the dissociation error of the conventional Hartree-Fock model is corrected through the use of the multi-configuration self-consistent-field (MC-SCF) approach. The specific configurations chosen in the MC-SCF ansatz introduce intraorbital correlation only, thus keeping the number of configurations small but yielding wave functions which permit proper dissociation into molecular fragments. An additional benefit is that for the presented model the variational solution of the orbital equations results in localized "chemical" orbitals. A set of atomic parameters for this model has been determined *via* least-squares fitting for the atoms C, H, O, and N. The model is applied to the calculation of molecular geometries, force constants, and heats of atomization of closed shell ground state molecules containing these atoms, giving results in good agreement with known experimental data.

This paper is the first in a series involving the development of a semiempirical method for the calculation of molecular systems of sufficient accuracy to be of chemical usefulness. To this end we feel the theory should be able to give reliable estimates of molecular geometries, heats of atomization, and force constants, as well as describing adequately bond formation and dissociation. If these objectives can be achieved, we then feel that we would have a quantum mechanical model useful for the study of a variety of reaction mechanisms. This should lead us to the prediction of transition species and selection of reaction paths.

Given these general expectations, the theory should be designed to make its interpretation on the basis of traditional chemical intuition as easy as possible. Since a semiempirical theory is built up from the standpoint that we know something about chemistry, it seems reasonable to expect that its output should lead to interpretation of chemical problems in those terms. For example, we believe that the bonding in molecules essentially involves the valence electrons, so we can then use a theory which treats the valence electrons explicitly and freezes the inner electrons as cores around the atomic nuclei. Furthermore, since we like to picture electrons as forming bond pairs between atoms, a theory which localizes electrons in this manner makes it convenient for the description of what is happening to reacting molecules in terms of these bonding electrons.

Pople's original development of the CNDO¹ semiempirical method was designed to be an approximation to a full LCAO-SCF minimal basis set calculation.

(1) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); **43**, S129 (1965).

That is, he designed the theory to reproduce a specific type of quantum mechanical calculation and not experimental data. However, the literature contains a number of proposals for modifying the theory to achieve agreement with various types of experimental information.² Dewar was one of the first to recognize the need for developing a method for general chemical usefulness. His MINDO³ procedure has been for the most part successful. However, the parameterization seems unnecessarily complicated in that the resonance integrals and core-core repulsions are treated with bond-dependent parameters. Another rather successful method has been developed by Fischer and Kollmar.⁴ Their theory remains uncomplicated requiring essentially a reparameterization of Pople's CNDO/2 method, but it has not been extended beyond hydrocarbons. A number of other modifications have been suggested but they do not appear to be applicable in meeting our general objectives. In particular, since all these theories are based on the HF model, they are afflicted with the well-known HF dissociation error; *i.e.*, if a bond is broken, the molecular fragments do not dissociate into their respective electronic ground states in the restricted HF model.

In this first paper we have attempted to keep the basic

(2) (a) K. B. Wiberg, *J. Amer. Chem. Soc.*, **90**, 59 (1968); (b) J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, **11**, 220, 254, 263 (1968); (c) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 4050 (1968); **49**, 1221 (1968).

(3) (a) N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5303 (1972); (b) M. J. S. Dewar and D. H. Lo, *ibid.*, **94**, 5296 (1972); (c) N. Bodor, M. J. S. Dewar, E. Haselbach, and A. Harget, *ibid.*, **92**, 3254 (1970); (d) M. J. S. Dewar and E. Haselbach, *ibid.*, **92**, 590 (1970).

(4) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **13**, 213 (1969).

theory as simple as possible to find out to what extent and in what areas improvements would be necessary. At this stage we are limiting ourselves to the atoms H, C, N, and O and the description of closed shell ground states. We have used Pople's CNDO/2 method with some changes in the approximation of penetration and resonance integrals. But instead of solving the single determinant Fock equations, we solve the MC-SCF⁵ equations for single and double pair replacement determinants. The parameterization we introduce has been optimized to obtain equilibrium geometries and heats of atomization for a selected set of molecules.

Perhaps we should say a few words about what solving the MC-SCF equations means for a theory at this level. In order to properly treat bond dissociation processes, it becomes necessary to use wave functions formed from a linear combination of Slater determinant instead of a single determinant. One way to do this would be to simply do a CI calculation. However, the disadvantage of that procedure is that one can only optimize the coefficients in the linear combination of determinants and not the molecular orbitals within the determinants. The MC-SCF procedure avoids this by simultaneously optimizing both sets of coefficients. By using only determinants corresponding to a transfer of pairs of electrons to bonding and antibonding orbitals, the MC-SCF equations become relatively simple and the electrons become localized into bond pairs. More important, however, with such a configuration selection the HF dissociation error is removed, and we can hope to adequately describe bond formation and bond breaking processes with our model.

In the next section we will outline the theoretical approach we have used. Next the optimization of the parameters is discussed and some initial results are presented. In the final section the theory is discussed from the point of view of the overall usefulness and its present limitations.

I. Theoretical Framework

We will now describe in some detail the formalism which has been developed to take into account single and double pair excitations from a closed shell reference determinant. Consider a set of M spatial, orthonormal orbitals

$$\{\phi_1, \phi_2, \dots, \phi_M\}$$

with M equal to the number of basis functions and N equal to the number of doubly occupied orbitals in the reference determinant, $M > N$. Let the ground state Slater determinant (SD) be represented by

$$\Phi_{00} = \{\phi_1^2, \phi_2^2, \dots, \phi_N^2\}$$

We can then construct the following normalized SD's

$$\Phi_{I0} = \{\phi_1^2, \dots, \phi_{i-1}^2, \phi_a^2, \phi_{i+1}^2, \dots, \phi_N^2\}$$

$$\Phi_{IJ} = \{\phi_1^2, \dots, \phi_{i-1}^2, \phi_a^2, \phi_{i+1}^2, \dots, \phi_{j-1}^2, \phi_b^2, \phi_{j+1}^2, \dots, \phi_N^2\}$$

where in Φ_{I0} orbital ϕ_a replaces ϕ_i and in Φ_{IJ} orbital ϕ_a replaces ϕ_i and ϕ_b replaces ϕ_j . These replacements are restricted so that each ϕ_i can only be replaced by one

(5) (a) J. Hinze, *J. Chem. Phys.*, **59**, 6424 (1973); (b) T. L. Gilbert, *Phys. Rev.*, **A6**, 580 (1972); (c) J. Hinze and C. C. J. Roothaan, *Progr. Theor. Phys.*, **40**, 37 (1967); (d) A. Veillard and E. Clementi, *Theor. Chim. Acta*, **7**, 133, 143 (1967).

and only one orbital ϕ_a , where ϕ_a is unoccupied in the reference determinant Φ_{00} . This restriction was made for the following reasons: (a) to keep the model relatively simple, (b) to give the theory a definite structure, (c) to permit proper treatment of bond dissociation, and finally (d) to yield orbitals which would be localized. If desired a final, more general CI could lift this restriction, but little can be expected from excitations $\phi_i^2 \rightarrow \phi_j^{*2}$ ($\phi_b = \phi_j^*$, the antibonding orbital to ϕ_j) since ϕ_i and ϕ_j^* are in different regions of space, while ϕ_i and ϕ_i^* (or ϕ_j and ϕ_j^*) occupy the same region of space. The total wave function can now be written as

$$\Psi = C_{00}\Phi_{00} + \sum_{I>J} C_{IJ}\Phi_{IJ}$$

Note that in this equation and all following ones the lower indices of the summations (J in this case) start at zero, unless otherwise specified.

For convenience we will divide the M spatial orbitals into three sets depending on their occupation in the total wave function. Orbitals which are doubly occupied in all SD's will be called core. Those which are doubly occupied in only some of the SD's will be called valence. Additional orbitals not used in the total wave function are called empty. These sets are designated by \mathcal{C} , \mathcal{V} , and \mathcal{E} , respectively.

Because we start with orthonormal orbitals, all the SD's will be orthonormal and the expectation value of the energy will be

$$E = \langle \Psi | \mathcal{H} | \Psi \rangle = C_{00}^2 \langle \Phi_{00} | \mathcal{H} | \Phi_{00} \rangle + 2C_{00} \sum_{I>J} C_{IJ} \langle \Phi_{00} | \mathcal{H} | \Phi_{IJ} \rangle + \sum_{\substack{I>J \\ K>L}} C_{IJ} C_{KL} \langle \Phi_{IJ} | \mathcal{H} | \Phi_{KL} \rangle$$

provided Ψ is normalized. Because of the restrictions made in constructing the SD's this expression simplifies to

$$E = C_{00}^2 E_{00} + 2C_{00} \sum_{I \neq 0} C_{I0} G_I + \sum_{I>J} C_{IJ}^2 E_{IJ} + 2 \sum_{\substack{I>J \\ J \neq 0}} [C_{IJ} (C_{I0} G_J + C_{J0} G_I)]$$

where

$$E_{IJ} = \langle \Phi_{IJ} | \mathcal{H} | \Phi_{IJ} \rangle$$

$$G_I = [ia|ia] = \langle \phi_i(1)\phi_a(2) | R_{12}^{-1} | \phi_a(1)\phi_i(2) \rangle$$

In order to come up with a compact notation we will write a general expression for E_{IJ} as

$$E_{IJ} = 2 \sum_k^M a_k^{IJ} \langle k|h|k \rangle + 2 \sum_{k,l}^M a_k^{IJ} a_l^{IJ} ([kk|ll] - 0.5[kl|kl])$$

where

$$a_k^{00} = \begin{cases} 1 & k \leq N \\ 0 & k > N \end{cases}$$

$$a_k^{I0} = \begin{cases} 1 & k \leq N, k \neq i \\ 0 & k \leq N, k = i \\ 0 & k > N, k \neq a \\ 1 & k > N, k = a \end{cases}$$

$$a_k^{IJ} = \begin{cases} 0 & k \leq N, k = i, j \\ 1 & k \leq N, k \neq i, j \\ 1 & k > N, k = a, b \\ 0 & k > N, k \neq a, b \end{cases}$$

This allows us to define the following effective coefficients

$$\begin{aligned} a_k &= 2 \sum_I C_{I0}^2 a_k^{I0} + 2 \sum_{I>J} C_{IJ}^2 a_k^{IJ} \\ b_{kl} &= 2 \sum_I C_{I0}^2 a_k^{I0} a_l^{I0} + 2 \sum_{I>J} C_{IJ}^2 a_k^{IJ} a_l^{IJ} \\ c_{kl} &= 1/2 [b_{kl} - 2\delta_{ik}\delta_{ia}(C_{00}C_{I0} + \sum_{J \neq I} C_{J0}C_{IJ}) - \\ &\quad 2\delta_{ka}\delta_{ia}(C_{00}C_{I0} + \sum_{J \neq I} C_{J0}C_{IJ})] \end{aligned}$$

where in the equation for c_{kl} I refers to the configuration of i replaced by a and δ is the Kronecker delta. This leads to the simple expression for the total energy

$$E = \sum_k^M a_k \langle k|h|k \rangle + \sum_{k,l}^M b_{kl} [kk|ll] - c_{kl} [kl|kl]$$

We can now write the Fock-like equations

$$F_i |\phi_i\rangle = \sum_j^M |\phi_j\rangle \epsilon_{ji}$$

where

$$F_i = a_i h + 2 \sum_j^M (b_{ij} J_j - c_{ij} K_j)$$

with

$$\begin{aligned} J_j |\phi\rangle &= \langle \phi_j | g | \phi_j \rangle |\phi\rangle \\ K_j |\phi\rangle &= \langle \phi_j | g | \phi \rangle |\phi_j\rangle \end{aligned}$$

The treatment of the pair-replacement formalism has thus far not required any approximations. But at this point we convert to the matrix form of the LCAO expansion and apply the CNDO approximation for the coulomb and exchange integrals.

That is, for molecular orbitals of the form

$$\phi_i = \sum_p \chi_p d_{ip}$$

the Fock matrix elements become

$$\begin{aligned} F_{i,pp} &= a_i H_{pp} - \left(\sum_j^M 2c_{ij} d_{jp}^2 \right) \gamma_{pp} + \sum_r^M \left[\left(\sum_j^M 2b_{ij} d_{jr}^2 \right) \gamma_{pr} \right] \\ F_{i,pq} &= a_i H_{pq} - \left(\sum_j^M 2C_{ij} d_{jp} d_{jq} \right) \gamma_{pq} \end{aligned}$$

since

$$\begin{aligned} J_{j,pq} &= \delta_{pq} \sum_r \gamma_{pr} d_{jr}^2 \\ K_{j,pq} &= \gamma_{pq} d_{jp} d_{jq} \end{aligned}$$

in the CNDO approximation, where γ_{pq} is determined solely from the atoms on which χ_p and χ_q reside. Notice the similarity of these equations to those used in the conventional CNDO method.

$$\begin{aligned} F_{pp} &= H_{pp} - \left(\sum_j^N d_{jp}^2 \right) \gamma_{pp} + \sum_r^M \left[\left(\sum_j^N 2d_{jr}^2 \right) \gamma_{pr} \right] \\ F_{pq} &= H_{pq} - \left(\sum_j^N d_{jp} d_{jq} \right) \gamma_{pq} \end{aligned}$$

Let us next address ourselves to the solution of the MC-SCF equations. Notice that we no longer have a simple eigenvalue problem with a single Fock operator but rather a set of coupled Fock equations. This coupling could be removed, at least formally, using projection operator techniques to yield a pseudo-eigenvalue equation.^{5a} However, in practice a solution based on the requirement of Hermiticity of the Lagrange multiplier matrix has been more successful. That is, we require ϵ_{ji} to equal ϵ_{ij} , with $\epsilon_{ij} = \langle \phi_i | F_j | \phi_j \rangle$.

Assume that we have a set of initial orbitals which do not in general satisfy our Fock equations. What we are looking for then is the unitary transformation which transforms these orbitals into a new set which does satisfy the equations. In matrix notation this becomes

$$\{\phi_1', \dots, \phi_M'\} = \{\phi_1, \dots, \phi_M\} \mathbf{U}$$

and we determine \mathbf{U} such that

$$\langle \phi_j' | F_i' | \phi_i' \rangle - \langle \phi_i' | F_j' | \phi_j' \rangle = 0$$

is satisfied for all i and j . Note that the indices i and j run over all orbitals including the empty set; however, $F_i = 0$ for $i \in \mathcal{E}$. While there are a number of possible ways to solve this equation,^{5a} the method we use is to approximate the unitary matrix as

$$\mathbf{U} = \mathbf{1} + \mathbf{V}$$

which is good to second order in terms of \mathbf{V} , provided \mathbf{V} is antisymmetric. This approximation requires that the initial orbitals are reasonably close to the solution orbitals. Using this approximation and neglecting the change in the Fock operators we get

$$\begin{aligned} \epsilon_{ji} - \epsilon_{ij} &\cong \langle \phi_j' | F_i | \phi_i' \rangle - \langle \phi_i' | F_j | \phi_j' \rangle \\ &= \sum_{m,n}^M U_{mj} \langle \phi_m | F_i | \phi_n \rangle U_{ni} - U_{mi} \langle \phi_m | F_j | \phi_n \rangle U_{nj} \\ &\cong \langle \phi_j | F_i | \phi_i \rangle - \langle \phi_i | F_j | \phi_j \rangle + \\ &\quad \sum_m^M [v_{mj} (\langle \phi_m | F_i | \phi_i \rangle - \langle \phi_i | F_j | \phi_m \rangle) + \\ &\quad v_{mi} (\langle \phi_j | F_i | \phi_m \rangle - \langle \phi_m | F_j | \phi_j \rangle)] = 0 \end{aligned}$$

These equations can now be collected into a set of linear equations

$$\sum_{m,n}^M R_{ij,mn} v_{mn} = g_{ij} \quad i > j; m > n; j, n \notin \mathcal{E}$$

This is possible because $v_{ij} = -v_{ji}$ and because we have neglected the second-order terms of \mathbf{V} . Note that ij and mn are composite indices, so that v and g are column vectors and \mathbf{R} is a square matrix. The reason j and n do not run over orbitals in the empty set is that rotations between orbitals in the empty set are not needed because they do not affect the wave function. The elements of g and \mathbf{R} are obtained as

$$\begin{aligned} g_{ij} &= \langle \phi_i | F_j | \phi_j \rangle - \langle \phi_j | F_i | \phi_i \rangle \\ R_{ij,mn} &= \delta_{mi} (\langle \phi_n | F_j | \phi_j \rangle - \langle \phi_j | F_i | \phi_n \rangle) + \\ &\quad \delta_{nj} (\langle \phi_m | F_i | \phi_i \rangle - \langle \phi_i | F_j | \phi_m \rangle) - \\ &\quad \delta_{ni} (\langle \phi_m | F_j | \phi_j \rangle - \langle \phi_j | F_i | \phi_m \rangle) - \\ &\quad \delta_{mj} (\langle \phi_n | F_i | \phi_i \rangle - \langle \phi_i | F_j | \phi_n \rangle) \end{aligned}$$

This set of linear equations is particularly well suited for solution by a dynamic Gauss-Seidel iterative method,⁶ since the off-diagonal elements of \mathbf{R} are small compared to the diagonal ones. The recurrence relation is

$$R_{ij,ij}\Delta v_{ij} = g_{ij} - \sum_{mn=1}^{ij-1} R_{ij,mn}v_{mn}^{(n)} - \sum_{mn=ij} R_{ij,mn}v_{mn}^{(n-1)}$$

$$v_{ij}^{(n)} = v_{ij}^{(n-1)} + \Delta v_{ij}$$

The procedure is started by assuming the initial $v_{ij}^{(0)}$'s are all zero and continued until the Δv_{ij} 's are less than some threshold.

At this point the steps necessary to do a typical calculation will be outlined. (1) A set of initial orbitals is chosen. These can be rather approximate but should be chosen on the basis of the bonds and lone pairs of the molecules. (2) For each bonding orbital an antibonding one is formed and these orbitals are used to form the corresponding SD's. (3) Then a CI calculation is performed to determine the coefficients C_{IJ} and the effective coefficients a_k , b_{kl} , and c_{kl} . (4) Next the Fock matrices F_i are calculated and the linear equations are solved to determine the v_{ij} 's. The old set of molecular orbitals is then transformed to the new set. Since we have neglected the change in the Fock matrices and the second-order terms of \mathbf{V} , it is necessary to repeat step 4 until the g_{ij} 's are less than a given threshold. (5) Finally, after step 4 converges we go back to step 3 and go through the procedure again until the difference in total energy of successive iterations is less than another threshold. We call step 4 the SCF cycle and step 5 to 3 the CI cycle. In the systems studied so far, convergence has been achieved usually in less than five CI iterations and a total of 25 SCF iterations, with an SCF threshold of 0.0001 and a CI threshold of 0.000001 hartree.

To complete the theoretical description let us specify how the coulomb integrals, γ_{pq} , and the core Hamiltonian matrix elements, H_{pq} , are to be determined. The coulomb integrals are found exactly as in Pople's CNDO, that is

$$\gamma_{pq} = \gamma_{AB} = [s_A s_A | s_B s_B]$$

where s_A and s_B are the valence s functions on those atoms. These functions are of the Slater type with the standard Slater exponents.

The Hamiltonian matrix elements were given by Pople as

$$H_{pp} = -1/2(I_p + A_p) - (Z_A - 0.5)\gamma_{AA} - \sum_{A>B} V_{AB} \quad (\chi_p \text{ on A})$$

$$V_{AB} = Z_B \gamma_{AB}$$

$$H_{pq} = 0 \quad (\chi_p, \chi_q \text{ on A, } p \neq q)$$

$H_{pq} = \beta_{pq} = 1/2(\beta_A^0 + \beta_B^0)S_{pq} \quad (\chi_p \text{ on A, } \chi_q \text{ on B})$

The values for the ionization potential I_p and the electron affinities A_p have been calculated from atomic data and we have used the values given by Pople.¹ However, we differ from CNDO/2 in the calculation of V_{AB} and β_{pq} .

Fischer and Kollmar⁴ noted that Pople's CNDO/2

(6) See, for example, R. S. Varga, "Matrix Iterative Analysis," Prentice-Hall, Edgewater Cliffs, N. J., 1962, p 58.

formalism as outlined above tended to yield high force constants. They found that the values of β_A^0 had little effect on the force constants and so found it necessary to alter V_{AB} . We have used their formula to calculate V_{AB}

$$V_{AB}^p = Z_B[(1 - \alpha)\gamma_{AB} + \alpha(R_{AB}^2 + (1/\zeta_p^2))^{-1/2}]$$

where α is a parameter and ζ_p is the orbital exponent for χ_p on atom A. The value for α is determined as a single quantity to be used for all A, B, and χ_p 's. This equation has given us improved force constants as well as giving more freedom in achieving optimal bond lengths.

The heats of atomization, bond lengths, and bond angles are affected by the value of the resonance integral β_{pq} . We tried to simply reparameterize Pople β_A^0 's but found that both single and multiple bond lengths could not be handled adequately to give also correct heats of atomization. Therefore, it was found necessary to introduce separate β 's for s and p basis functions, using the same distance dependence as Pople.

$$\beta_{pq} = 0.5(\beta_p + \beta_q)S_{pq}$$

The theory is no longer invariant to hybridization, but this seems to make little difference in the total energies.⁷ A number of people have used Mulliken's approximation

$$\beta_{pq} = \beta_{AB}(I_p + I_q)S_{pq}$$

which is similar to our form. However, we found that this approximation yielded poor bond angles in our model if average valence state ionization potentials were used.

II. Optimization of Parameters

In order to do calculations on molecules containing H, C, N, and O, we must specify eight parameters (α , β_H , β_C^s , β_C^p , β_N^s , β_N^p , β_O^s , and β_O^p). To do this we selected seven molecules, H_2 , CH_4 , C_2H_2 , H_2O , CH_2O , NH_3 , and N_2 , on the basis that they were representative of single and multiple bonding for these atoms and were easy to calculate. All the calculations were done using determinants formed with both single and double pair excitations. However, at the equilibrium geometries the expansion coefficients of determinants corresponding to double pair excitations are all small, usually less than 0.02. These double excitations will become important only as a bond is dissociated.

The parameters were then determined using a least-squares fit to the experimental values of 18 observables, including the bond lengths and heats of atomization of all these molecules, the HOH angle in H_2O , and the HNH angle in NH_3 . The minimum in this least-squares fit was found to be rather shallow, leading to slow convergence. The final set of β 's obtained, averaged from two least-squares iterations, is listed in Table I. The value for α was found to be 0.3143.

Table I. Parameters for H, C, N, O (au)

	H	C	N	O
$-\beta^s$	0.2923	0.5404	0.7673	0.9885
$-\beta^p$		0.3795	0.5034	0.8282

(7) D. T. Clark, *Theor. Chim. Acta*, 10, 111 (1968).

Table II. Heats of Atomization (au)

	Exptl	Calcd	$E_o - E_x$	$(E_o - E_x)/E_x, \%$
H ₂	0.174	0.191	0.017	9.77
CH ₄	0.669	0.656	-0.013	-1.94
C ₂ H ₂	0.647	0.655	0.008	1.24
C ₂ H ₄	0.897	0.874	-0.023	-2.56
C ₂ H ₆	1.134	1.089	-0.045	-3.97
C ₃ H ₆	1.368	1.298	-0.069	-5.04
H ₂ O	0.370	0.373	0.003	0.81
CH ₂ O	0.597	0.611	0.014	2.35
CH ₃ OH	0.815	0.824	0.009	1.10
N ₂	0.363	0.386	0.023	6.34
NH ₃	0.475	0.463	-0.012	-2.53
CH ₃ NH ₂	0.927	0.896	-0.031	-3.34
HCN	0.498	0.496	-0.002	-0.40
H ₂ O ₂	0.427	0.590	0.163	38.17
HCOOH	0.797	0.790	-0.007	-0.88
Mean absolute error ^a			0.020	3.02
Mean error ^a			-0.009	0.07
Standard deviation ^{a,b}			0.026	4.06

^a Excluding H₂O₂. ^b $S = [(\sum x_i^2 - (\sum x_i)^2/N)/(N-1)]^{1/2}$.

Table III

	Bond lengths, Å				Force constants, mdyn/Å				
	Exptl	Calcd	$R_o - R_x$	$(R_o - R_x)/R_x, \%$	Exptl	Calcd	$f_o - f_x$	$(f_o - f_x)/f_x, \%$	
H—H	H ₂	0.741	0.716	-0.025	-3.37	5.7	7.5	1.8	31.6
C—H	CH ₄	1.093	1.097	0.004	0.37	5.4	7.7	2.3	42.6
	C ₂ H ₂	1.059	1.073	0.014	1.32	6.2	8.5	2.3	37.1
	C ₂ H ₄	1.086	1.094	0.008	0.74	5.1	7.7	2.6	51.1
	C ₂ H ₆	1.093	1.103	0.010	0.91	4.8	7.5	2.7	56.3
	CH ₂ O	1.120	1.104	-0.016	-1.43	5.3	6.5	1.2	22.6
O—H	HCN	1.063	1.076	0.013	1.22	5.9	8.3	2.4	40.7
	H ₂ O	0.957	0.988	0.031	3.24	7.8	14.2	6.4	82.1
	CH ₃ OH	0.960	0.990	0.030	3.13	7.6	13.9	6.3	82.9
N—H	H ₂ O ₂	0.950	0.999	0.049	5.16	8.4	15.0	6.6	78.6
	NH ₃	1.014	1.039	0.025	2.47	6.4	10.5	4.1	64.1
	CH ₃ NH ₂	1.014	1.046	0.032	3.16	6.3	10.3	4.0	63.5
C—O	CH ₃ OH	1.428	1.359	-0.069	-4.83	5.4	7.5	2.1	38.9
	HCOOH	1.312	1.345	0.033	2.52	6.1	13.3	7.2	118.0
C=O	CH ₂ O	1.210	1.223	0.013	1.07	12.3	18.5	6.2	50.4
	HCOOH	1.245	1.238	-0.007	-0.06	11.6	15.8	4.2	36.2
C—C	C ₂ H ₆	1.534	1.535	0.001	0.07	4.5	6.2	1.7	37.8
	C ₃ H ₆	1.488	1.507	0.019	1.28		12.7		
	C ₂ H ₄	1.337	1.341	0.004	0.30	9.6	10.9	1.3	13.5
C≡C	C ₂ H ₂	1.353	1.361	0.008	0.59		10.1		
	C ₂ H ₂	1.205	1.189	-0.016	-1.33	15.8	16.0	0.2	1.3
C—N	CH ₃ NH ₂	1.474	1.462	-0.012	0.81	5.0	6.9	1.9	38.0
	HCN	1.155	1.166	0.011	0.95	17.9	20.6	2.7	15.1
O—O	H ₂ O ₂	1.475	1.210	-0.265	17.97	4.0	19.5	15.5	387.5
	N ₂	1.095	1.122	0.027	2.47	23.0	28.4	5.4	23.5
Mean absolute error ^a			0.020	1.78			3.44	46.63	
Mean error ^a			0.008	0.78			3.44	46.63	
Standard deviation ^a			0.024	2.18			2.06	27.04	

^a Excluding O—O in H₂O₂.

III. Results

In Table II we have compared the calculated and experimental heats of atomization of the seven molecules used in the parameterization and eight additional molecules. The additional eight molecules were calculated with the fitted parameter set in order to test whether the determined parameters are generally applicable outside the set of molecules used in the optimization. Excluding H₂O₂ which we will discuss below, the average magnitude of the error is about 3% of the total heat of atomization. However, errors of this magnitude are still rather large when considering chemical reactions where 0.01 hartree corresponds to about 6.3 kcal/mol. The fact that the errors are not all

of the same sign is particularly unfortunate in that there is little chance of cancellation of errors in a reacting system.

The agreement of our calculated bond lengths and angles with the experimental values is very satisfactory. These are listed in Tables III and IV. Also listed in Table III are the force constants for bond stretching. Except for H₂O₂ and the CO bond in CH₃OH all bond lengths are reproduced within 0.035 Å. In the case of CH₃OH the calculated value is 0.069 Å less than the observed length. Note that MINDO/2^{3c} also has difficulty with this bond, being too short by 0.054 Å. As Dewar has discussed, the problem in H₂O₂ is due to the neglect of two-electron integrals involving one-center overlap in these methods. This causes the exchange repulsions between lone pairs to be underestimated and the corresponding bonds become too short and molecular energies too low. On the whole, however, the accuracy in the prediction of bond length is very

Table IV. Bond Angles (deg)

	Exptl	Calcd	$\theta_o - \theta_x$	$(\theta_o - \theta_x)/\theta_x, \%$	
∠HCH	C ₂ H ₄	115.5	112.4	-3.1	-2.68
	CH ₂ O	118.0	114.8	-3.2	-2.71
∠HOH	H ₂ O	104.5	107.3	2.8	2.68
∠HNH	NH ₃	106.8	109.7	2.9	2.72
Mean absolute error				3.00	2.70
Mean error				-0.15	0.01
Standard deviation				3.46	3.11

pleasing. Notice that we have not had to make any special provisions for the bonding of hydrogen to second-row atoms as is done in MINDO/2, where these

bonds must be offset between 0.1 and 0.15 Å. Bond angles are also given well with errors usually less than 4°.

However, force constants are on the order of 50% too high. While this is somewhat regrettable, we have reduced the CNDO/2 values which are from two to three times the experimental values. There is some satisfaction in that our values seem consistent in that trends within and between groups of bonding pairs are reproduced. For example, as we go from C₂H₂ to C₂H₄ to C₂H₆ the C–H force constants decrease and in going from C–H to N–N to O–H the force constants increase, as they should.

At this point we would like to compare the results of this MC-SCF approach with those for a single determinant using the same parameters. For the molecules calculated in this paper, the equilibrium geometries are predicted with about the same accuracy with either the single or multiconfiguration approach. The force constants were improved between 6 and 10% with the MC-SCF method. And, of course, the calculated heats of atomization are too small for the single determinant case, since the parameter optimization took into account the CI energy, which ranged from 0.027 to 0.125 au. It seems likely that by using the formulas for β_{pq} and V_{AB} given in this paper and a different set of optimized parameters one could get results comparable to ours for equilibrium geometry calculations using only a single determinant. However, it should be emphasized that the principle advantage of this MC-SCF approach is that it allows potential curves to be calculated up to the dissociation limit, which cannot be done using any single determinant Hartree-Fock method.

IV. Conclusion

As was stated in the introduction our objective is to

develop a semiempirical model accurate enough to be of use in chemical problems. Clearly at this early stage we still have a way to go. However, it is encouraging that we have been able to do as well as we have with only eight parameters and by neglecting all differential overlap in two-electron integrals. While MINDO/2 presently gives more accurate results for heats of atomization and force constants, it requires 20 parameters and calculation of integrals involving monatomic differential overlap.

To improve our model it is particularly important to predict heats of atomization more reliably. Perhaps a different form of V_{AB} is necessary. Another possibility is the inclusion of integrals used in the INDO approximation. However, these changes are of a minor nature and fit easily in the MC-SCF pair-replacement formalism. More restrictive at the present time is the fact that we can only treat closed shell systems. Another limitation is that the model does not conveniently handle delocalized electrons as occur in aromatic systems. The difficulty with bonds between two atoms with lone pairs is perhaps not too serious given the few molecules involved.

It seems reasonable that these improvements can and will be made to this MC-SCF procedure. The flexibility in adequately treating a variety of reactions processes and the ease of interpreting "chemically" localized orbitals makes this approach particularly appealing and useful.

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Mechanisms of Spin Delocalization. An Experimental Study of γ and δ Proton Contact Shifts

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Abstract: Nickel-induced pmr contact shifts have been determined for the γ and δ protons of a variety of amines in which the molecular geometries are constrained to rigidly fixed conformations. For γ protons, it is concluded that homohyperconjugation, which places α spin at the protons in question, is dominant for those protons obeying the W plan. This mechanism falls off approximately as $\cos^6 \theta_{\gamma^H}$ and allows spin polarization to dominate for a wide range of conformations, resulting in β spin at the protons. Finally, for protons in the conformation $\theta_{\beta^C} = 0^\circ$ and $\theta_{\gamma^H} = 0^\circ$, another resonance contribution leads to small positive spins. For δ hydrogens, the largest positive spin densities result for those protons in the W-plan geometry and are attributed to an extended σ -bond resonance phenomenon. Smaller spin densities are induced at δ protons not conforming to the W plan.

The subject of spin delocalization in organic free radicals has attracted considerable attention in recent years. An understanding of this subject is naturally of value in interpreting esr spectroscopic data, but a further incentive for elucidating these mechanisms has been provided by the recent recognition that the chemical behavior of both open and closed shell sys-

tems is intimately associated with the spin density distributions in related radicals.¹⁻³ Epiotis,² for ex-

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