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The MNDOC Method, a Correlated Version of the MNDO Model

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Abstract: Explicit inclusion of electron correlation into the MNDO model leads to the semiempirical MNDOC method which is parametrized for the elements H, C, N, and O. Correlation is treated in MNDOC by second-order Brillouin–Wigner perturbation theory with Epstein–Nesbet energy denominators, although it is shown that configuration interaction approaches can also be applied with the use of unmodified MNDOC parameters. Calculated heats of formation and geometries for closed-shell ground states are of similar accuracy in MNDOC and MNDO which is rationalized by an analysis of the MNDOC correlation effects in these systems.

Current semiempirical methods designed for the study of potential surfaces (e.g., CNDO/2,[1] MINDO/3,[2] MNDO[3]) are derived from the Roothaan–Hall[4,5] SCF–LCAO–MO treatment by suitable integral approximations. Being simplified versions of the Hartree–Fock method, they do not include electron correlation explicitly. In MINDO/3 and MNDO, it is hoped that the semiempirical reduction of the two-electron integrals and the parametrization account for correlation effects in an average manner. However, specific correlation effects cannot be included in this way, and it is not obvious how to estimate their magnitude in specific cases. Applications of MINDO/3 and MNDO have therefore often been met with skepticism.

In this situation, it would certainly be desirable to develop a correlated semiempirical method for the study of potential surfaces. The present paper reports a reparametrization of the MNDO model with explicit inclusion of electron correlation, the resulting treatment being named MNDOC (C for correlation). The paper also describes the MNDOC results for closed-shell ground states, whereas the following two papers deal with reactive species, transition states, and excited states.

Theoretical Approach

Electron correlation can be treated by a variety of methods,[6] among them configuration interaction (CI),[7-9] pair theories,[10] many-body perturbation theory,[11,12] conventional perturbation theory,[10,13-15] and CI perturbation theory (PERTCI).[16] The choice of a correlation treatment for MNDOC is based on the criterion that all correlation effects should be included in a consistent and efficient manner. The most suitable treatment will thus be the one which approximates the exact MNDOC correlation energy as closely and efficiently as possible. This concept of aiming at the exact solution of the semiempirical model Hamiltonian is in the spirit of the recent LNDO/S method[17] which has been designed for spectroscopic studies.

The exact correlation energy for a given basis set is provided by a full CI treatment involving all configurations that can be generated. It is approximated by a double excitation configuration interaction (DECI)[7,18] including all configurations which are singly or doubly excited relative to the SCF configuration. Both CI treatments fulfill the formal requirements for a "theoretical model chemistry"[15] (except that DECI is not size consistent), but they are too expensive to be applied to larger molecules. Under these circumstances, the PERTCI method[16] is appealing since it is more economical, allows for a systematic approach to the exact correlation energy,[16] and has already been applied successfully in LNDO/S;[17] however, even PERTCI is slower than is desirable for the study of potential surfaces. Therefore CI calculations via the PERTCI program system[16] will mainly be used for reference purposes in MNDOC studies of ground states.

Second-order perturbation approaches are the fastest correlation treatments available, and are thus particularly attractive for semiempirical models. The variants of second-order perturbation theory[10-15] differ in using the Rayleigh–Schrödinger (RS) or Brillouin–Wigner (BW) expansions combined either with Møller–Plesset (MP)[19] or with Epstein–Nesbet (EN)[20,21] energy denominators. Each of these variants has its own merits and demerits.[10-15] From a formal point of view, RSMP would seem preferable because the RS approach is size consistent (contrary to BW) and because the MP results are invariant to unitary transformations between degenerate orbitals (contrary to EN). However, within the MNDOC framework, the RSMP correlation energies typically amount only to about 60% of the DECI ones, whereas RSEN and BWEN usually recover about 90–110%. This is due to the fact that the second-order EN treatment includes higher order terms of the MP treatment.[13] Alternatively, BWEN can be regarded as an approximate CI treatment since it is equivalent to the diagonalization of a CI matrix which has nonzero elements only on the diagonal, in the first row, and in the first column. Therefore it is not surprising that BWEN reproduces the DECI correlation energies even better than RSEN and is the best perturbation variant in this respect.[14,16]

In choosing a correlation treatment for closed-shell ground states in MNDOC, BWEN thus seems to be the best compromise since it is fast and provides a close approximation to the exact MNDOC correlation energy. We shall therefore treat electron correlation in the MNDOC parametrization and in standard applications by

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(1) Pople, J. A.; Segal, G. A. *J. Chem. Phys.* **1966**, *44*, 3289.
(2) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.
(3) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(4) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.
(5) Hall, G. G. *Proc. R. Soc. London, Ser. A* **1951**, *205*, 541.
(6) Schaefer, H. F., III, Ed. "Modern Theoretical Chemistry. Electronic Structure Theory"; Plenum Press: New York, 1977; Vol. 3.
(7) Shavitt, I. Reference 6; Chapter 6.
(8) Roos, B. O.; Siegbahn, P. E. M. Reference 6; Chapter 7.
(9) Meyer, W. Reference 6; Chapter 11.
(10) Kutzelnigg, W. Reference 6; Chapter 5.
(11) Freed, K. F. *Annu. Rev. Phys. Chem.* **1971**, *22*, 313.
(12) Bartlett, R. J.; Silver, D. M. *J. Chem. Phys.* **1975**, *62*, 3258.
(13) Claverie, P.; Diner, S.; Malrieu, J. P. *Int. J. Quantum Chem.* **1967**, *1*, 751.
(14) Ostlund, N. S.; Bowen, M. F. *Theor. Chim. Acta* **1976**, *40*, 175.
(15) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.
(16) Hase, H. L.; Lauer, G.; Schulte, K.-W.; Schweig, A. *Theor. Chim. Acta* **1978**, *48*, 47.
(17) Lauer, G.; Schulte, K.-W.; Schweig, A. *J. Am. Chem. Soc.* **1978**, *100*, 4925.
(18) Davidson, E. R. In "The World of Quantum Chemistry"; Daudel, R., Pullman, B., Eds.; Reidel: Dordrecht, 1974.
(19) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(20) Epstein, P. S. *Phys. Rev.* **1926**, *28*, 695.
(21) Nesbet, R. K. *Proc. R. Soc. London, Ser. A* **1955**, *230*, 312, 322.

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second-order BWEN perturbation theory, and the term "MNDOC results" without further specification will refer to MNDOC BWEN calculations, in the case of ground states.

It should be pointed out, however, that MNDOC does not necessarily involve a BWEN treatment of correlation. According to a subsequent analysis (see Results), it is justified to carry out MNDOC CI calculations with unmodified MNDOC parameters. The present MNDOC parametrization is thus valid in conjunction with any correlation treatment which closely approximates the exact MNDOC correlation energy. In particular, this allows the use of the PERTCI treatment,[16] which is the method of choice for excited states.

Having defined our basic theoretical approach, we shall now turn to some details concerning the MNDOC SCF procedure, the integral transformation, and the correlation treatments used.

A MNDOC calculation starts with a standard closed-shell SCF calculation. The MNDOC integral approximations and parametric functions are the same as those in MNDO[3,22] with two minor improvements in the two-electron integrals. In MNDO, the one-center integrals h_{pp} are given as data rounded to two decimal places,[2,3] and the two-center integrals $(p_x{}^A p_y{}^A, p_x{}^B p_y{}^B)$ are evaluated according to the multipole model.[22] In MNDOC, these two types of integrals are computed from the symmetry relations between the appropriate Coulomb integrals[23] which ensures strict rotational invariance in MNDOC.[24]

The MNDOC SCF calculation is followed by the transformation of the two-electron AO integrals $(\mu\nu, \lambda\sigma)$ to MO integrals (ij, kl). For CI, all integrals (ij, kl) must be computed, whereas only a subset of these integrals is needed for BWEN. The transformation is carried out in two summations over the index pairs $(\mu\nu)$ and $(\lambda\sigma)$ which replace four summations over single indices in the ab initio case. This simplification is feasible due to the integral approximations in MNDOC since there are typically only $2N$ nontrivial index pairs for N basis AOs.

In the second-order BWEN treatment, the correlation energy E^{BWEN} is obtained in eq 1 by summing the contributions from all

$$E^{\mathrm{BWEN}} = -\sum_k \frac{|V_{k0}|^2}{E_k - (E_0 + E^{\mathrm{BWEN}})} \tag{1}$$

spin and symmetry adapted, doubly excited configurations Ψ_k where V_{k0} is the matrix element of the perturbation, E_k the Hartree–Fock energy of the configuration Ψ_k, and E_0 the Hartree–Fock energy of the SCF configuration Ψ_0. Explicit formulas for V_{k0} and E_k in terms of MO integrals and orbitals energies are available in the literature (e.g., see ref 14), and thus will not be repeated here.[25] Equation 1 is solved iteratively; after starting with $E^{\mathrm{BWEN}} = 0$, convergence is reached typically in 5–10 iterations.

Special problems with BWEN occur for systems with degenerate orbitals since the BWEN energy is not invariant to unitary transformations among degenerate orbitals,[14,15] the resulting energy changes being of the order of 0.1 kcal/mol in MNDOC. So that a unique definition of the BWEN energy in these cases could be ensured, the following convention is introduced: any degenerate MOs are transformed such that they conform to the symmetry of a point group with nondegenerate irreducible representations only (e.g., $D_{\infty h} \rightarrow D_{2h}$, $C_{3v} \rightarrow C_s$, etc.).

MNDOC DECI calculations are carried out in the standard manner.[7,16] The correlation energy E^{DECI} and the eigenvector $\mathbf{C}^{\mathrm{DECI}}$ are obtained from the lowest root of the DECI matrix $\mathbf{H}^{\mathrm{DECI}}$ involving all singly or doubly excited, spin and symmetry adapted configurations.

Table I. MNDOC Computation Times[a]

molecule	symmetry[b]	N[c]	N_{conf}[d]	SCF	BWEN	DECI
C_2H_4	D_{2h}	12	118	1.0	0.2	4.9
$CH_3CH_2CH_3$	C_{2v}	20	1334	1.0	0.6	68.4
C_6H_6	$D_{6h} \rightarrow D_{2h}$	30	6397	1.0	1.8	~600[e]
$C_{18}H_{18}$	$D_{3h} \rightarrow C_{2v}$	90	580050	1.0	22.9	

[a] Relative to the time for an SCF calculation. [b] $D_{6h} \rightarrow D_{2h}$, etc.: the molecule has D_{6h} symmetry, while the MOs and the configurations are adapted to D_{2h} symmetry (see Theoretical Approach). [c] Number of basis AOs. [d] Number of spin and symmetry adapted, doubly excited configurations. [e] Estimated by extrapolation.

Table II. Standard Molecules and Reference Properties for MNDOC Parametrization

molecule	ΔH_f[a]	gradient[b]	molecule	ΔH_f[a]	gradient[b]
H_2	X	X	CH_3CN	X	X
CH_4	X	X	$(CN)_2$	X	
C_2H_6	X	X	H_2O	X	X
C_2H_4	X	X	CH_3OH	X	X
C_2H_2	X	X	$(CH_3)_2O$	X	X
cyclopropane	X		oxirane	X	
cyclobutane	X		H_2O_2	X	X
benzene	X		O_3	X	
N_2	X	X	CO	X	X
NH_3	X	X	CO_2		
CH_3NH_2	X	X	H_2CO	X	X
$(CH_3)_2NH$	X		$(CH_3)_2CO$	X	
aziridine	X		CH_2CO	X	X
N_2H_4	X	X	HCOOH	X	
HCN	X	X			

[a] Heat of formation. [b] Gradient of the energy with respect to a geometrical variable. For each of the molecules marked, all independent gradient components are included as reference properties.

Table III. Optimized MNDOC Parameters

parameter	H	C	N	O
U_{ss}, eV	−12.113619	−51.856 594	−70.348 077	−99.400 519
U_{pp}, eV		−39.306 788	−57.350 327	−77.268 163
ζ, au	1.359938	1.828 090	2.295 131	2.733 991
β_s, eV	−6.929584	−15.235 343	−20.129 705	−32.722 231
β_p, eV		−10.297 988	−20.129 705	−32.722 231
α, Å^{-1}	2.592386	2.550 031	2.857 123	3.168 422

$$\mathbf{H}^{\mathrm{DECI}}\mathbf{C}^{\mathrm{DECI}} = E^{\mathrm{DECI}}\mathbf{C}^{\mathrm{DECI}} \tag{2}$$

The exact correlation energy from a full CI treatment is estimated with use of the Davidson correction[18]

$$E^{\mathrm{CI}} \approx E^{\mathrm{DECI}}[2 - (\mathbf{C}^{\mathrm{DECI}}{}_0)^2] \tag{3}$$

where $\mathbf{C}^{\mathrm{DECI}}{}_0$ is the coefficient of the SCF configuration in the DECI vector. This approximation has been established to account quite accurately for the effects of the higher excitations.[26-28]

Computational Aspects

For a molecule with N basis AOs and n occupied MOs, the computation time can be shown[14,29] to be proportional to N^3 for the MNDOC SCF calculation, to nN^4 for the BWEN integral transformation, to N^5 for the DECI integral transformation, to n^2N^2 for the BWEN treatment, and to n^4N^2 for the DECI treatment. Hence, the integral transformation is the time-determining step in MNDOC BWEN but not in MNDOC DECI.

Apparently, MNDOC DECI is 1 order of N more difficult than

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(22) Dewar, M. J. S.; Thiel, W. *Theor. Chim. Acta* **1977**, *46*, 89.

(23) Roothaan, C. C. J. *J. Chem. Phys.* **1951**, *19*, 1445.

(24) The MNDO energy may change very slightly during a rotation (typically by 0.01 kcal/mol) since the symmetry relations mentioned are not fulfilled. In practice, this does not matter in geometry optimizations, due to the geometry conventions in the standard programs, e.g.: Thiel, W. *QCPE* **1978**, *11*, 353.

(25) The two linearly independent singlets generated by the double excitation $ij \rightarrow uv$ are chosen to be defined in the same way as in ref 14; however, no 2 × 2 diagonalizations are performed in the summation process.[14]

(26) Bartlett, R. J.; Shavitt, I. *Chem. Phys. Lett.* **1977**, *50*, 190.

(27) Davidson, E. R.; Silver, D. W. *Chem. Phys. Lett.* **1977**, *52*, 403.

(28) Siegbahn, P. E. M. *Chem. Phys. Lett.* **1978**, *55*, 386.

(29) Davidson, E. R. In "Energy, Structure and Reactivity"; Smith, D. W., McRae, W. B., Eds.; Wiley: New York, 1973.

Table IV. Derived MNDOC Parameters

parameter	H	C	N	O
ΔH_f^A, kcal mol^{-1}	52.102	170.89	113.00	59.559
E_{el}^A, eV	−12.113 619	−119.856 764	−199.932 135	−315.263 690
D_1, Å		0.417 806	0.332 786	0.279 367
D_2, Å		0.354 520	0.282 378	0.237 051
ρ_0, Å	0.560 345	0.588 660	0.529 751	0.466 882
ρ_1, Å		0.424 987	0.334 133	0.273 949
ρ_2, Å		0.389 735	0.321 720	0.276 222

Table V. Mean Absolute Errors for Heats of Formation (kcal/mol)[a]

class of compds	N[b]	MNDO[c]	MNDOC
all compds	64	6.2	5.3
hydrocarbons	27	4.4	4.7
Acyclic	21	3.5	3.8
Cyclic	6	7.9	7.8
nitrogen compds (CHN)	16	5.9	5.2
oxygen compds (CHO)	18	7.3	5.0
nitrogen–oxygen compds (CHNO)	3	15.9	12.7

[a] On the basis of the results of Table VI. [b] Number of comparisons. [c] The present MNDO statistics differ slightly from previous ones[37] due to the use of a smaller set of test molecules.

MNDOC BWEN, which in turn is 2 orders of N more expensive than MNDOC SCF. This comparison, however, is somewhat misleading, especially with regard to BWEN vs. SCF. For a hydrocarbon molecule C_mH_{2m}, e.g., the BWEN integral transformation involves approximately $5N^5/32$ multiplications, or even less in the case of symmetry. On the other hand, the SCF treatment requires typically about $15N^3$ multiplications, assuming 9 SCF iterations each of which takes at least $5N^3/3$ multiplications for matrix diagonalization.[30] As a consequence, the MNDOC SCF and BWEN treatments usually are of comparable speed up to $N = 30$. This is obvious from Table I which gives actual SCF, BWEN, and DECI computation times.

BWEN calculations for large molecules do not present any particular problems, in principle, since the MO integrals can be generated in the same sequence as they are used in the perturbational summation ($N = 90$ is the largest case studied yet). DECI calculations, however, are limited by the size of the DECI matrix that can be handled. With use of methods specifically designed for the diagonalization of large sparse matrices,[7,31] dimensions of several thousand configurations are possible. Accordingly, DECI calculations seem to be practical up to $N = 25$, i.e., in MNDOC for molecules with at most four nonhydrogen atoms.

MNDOC SCF geometry optimizations are very efficient because the gradient of the energy with respect to the geometrical variables is easily evaluated for variationally optimized SCF wave functions.[32,33] In BWEN and DECI treatments, the energy is no longer stationary with respect to the LCAO coefficients so that the gradient components must be computed inefficiently by finite difference. Consequently, geometry optimizations for MNDOC BWEN and MNDOC DECI are significantly more expensive than for MNDOC SCF (see ref 34 for a more detailed analysis). In practice, MNDOC BWEN optimizations seem to be feasible for systems with five nonhydrogen atoms (MNDOC DECI, two nonhydrogen atoms). For larger molecules, it is therefore inevitable to use SCF optimized geometries in MNDOC studies which we shall demonstrate to be a reasonable approximation (see Results).

Parametrization

The MNDOC formalism contains the same adjustable atomic SCF parameters that are used in MNDO,[3] without any additional parameters due to the correlation treatment. The MNDOC parameters are determined by fitting the experimental values Y_l of L properties of the standard molecules used in the parametrization. This is done by minimizing the sum Y of the squares of the weighted errors ΔY_l in the calculated values

$$Y = \sum_{l=1}^{L}(\Delta Y_l)^2 = \sum_{l=1}^{L}[Y_l(\text{calcd}) - Y_l(\text{obsd})]^2 W_l^2 \qquad (4)$$

where W_l is a weighting factor for the quantity Y_l.

The MNDOC parametrization was carried out in analogy to the MNDO one with use of a nonlinear least-squares optimization procedure.[35] Since the MNDO parametrization has been described in detail,[3] we shall presently only remark on some essential aspects of the MNDOC parametrization and refer to our previous discussion[3] for further information.

During the MNDOC parametrization, electron correlation was treated by second-order BWEN perturbation theory. The reference properties Y_l for the standard molecules (see Table II) included heats of formation and geometrical variables. All calculations were carried out at the experimental geometries. Since the gradients of the energy with respect to the geometrical variables were minimized, the parameters were adjusted to reproduce equilibrium structures without optimizing molecular geometries. The weighting factors W_l were the same as previously.[3]

The standard molecules (Table II) were divided into three groups, namely, hydrocarbons, CHN systems, and CHO systems. Each group contained about 10 molecules and was parametrized separately. The parameters for C and H were first determined from the hydrocarbon group; these were then taken as constants in the parametrizations for N and O from compounds of the two other groups.

The MNDOC parametrization differed from the MNDO one only in three minor aspects due to the attempt to save computational effort: the MNDOC parameters were not refined in a parametrization run using optimized geometries, three molecules from the MNDO list of standard molecules were omitted in the MNDOC list, and the MNDOC reference properties did not include ionization potentials or dipole moments (cf. Table I in ref 3). None of these simplifications was expected to produce significant effects on the values of the parameters. Note, in particular, that the ionization potentials and dipole moments had provided only a small contribution to the Y value in the MNDO parametrization due to the choice of the weighting factors.[3]

Therefore we do believe that the parameters in MNDOC and in MNDO have been determined with similar accuracy. Comparisons between MNDOC and MNDO results will thus not be marred by technical inadequacies in one of the two parameter sets but will rather reveal the influence of the underlying theoretical model on the results.

Table III shows the optimized MNDOC parameters, i.e., the one-center energies U_{ss} and U_{pp}, the orbital exponents ζ, the resonance parameters β_s and β_p ($\beta_s = \beta_p$ for N, O), and the core–core repulsion parameters α. Table IV contains the derived[3] MNDOC parameters which include the experimental heats of formation ΔH_f^A of the atoms, the electronic energies E_{el}^A of the atoms, and the charge separations D_l and additive terms ρ_l used in the multipole model for the two-center, two-electron integrals.[22]

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(30) Wilkinson, J. H. "The Algebraic Eigenvalue Problem"; Oxford University Press: London, 1965; Chapter 5.

(31) Davidson, E. R. *J. Comput. Phys.* **1975**, *17*, 87.

(32) McIver, J. W.; Komornicki, A. *Chem. Phys. Letters* **1971**, *10*, 303.

(33) Pulay, P. In "Modern Theoretical Chemistry. Electronic Structure Theory"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 4, Chapter 4.

Table VI. Heats of Formation (kcal/mol) for Closed-Shell Molecules[a]

molecule	MNDO	MNDOC	MNDOC BWEN/SCF	MNDOC DECI/SCF	MNDOC CI/SCF	exptl	ref
H_2	0.7	1.7	1.8	1.8	1.8	0.0	
CH_4	−11.9	−11.9	−11.8	−12.7	−12.8	−17.9	*b*
C_2H_6	−19.7	−20.2	−20.1	−22.3	−22.6	−20.2	*b*
C_2H_4	15.3	15.7	16.0	14.6	13.7	12.5	*b*
C_2H_2	57.3	54.2	54.9	55.4	54.5	54.3	*b*
$CH_3CH_2CH_3$	−24.9	−25.7	−25.6	−29.2	−29.8	−24.8	*b*
$CH_3CH{=}CH_2$	4.9	5.1	5.3	2.5	1.1	4.9	*b*
$CH_3C{\equiv}CH$	40.9	37.7	38.5	37.0	35.6	44.4	*b*
$CH_2{=}C{=}CH_2$	43.8	44.7	45.1	42.7	40.6	45.6	*b*
n-butane	−29.7	−30.4	−30.3	−35.5	−36.6	−30.4	*b*
isobutane	−26.8	−27.7	−27.5			−32.4	*b,l*
1-butene	0.3	0.7	1.0	−3.5	−5.5	−0.2	*b*
trans-2-butene	−5.1	−4.9	−4.6	−9.4	−11.4	−3.0	*b*
cis-2-butene	−4.0	−3.9	−3.5	−8.2	−10.2	−1.9	*b*
isobutene	−2.1	−1.9	−1.6	−6.0	−8.0	−4.3	*b*
1,2-butadiene	33.4	34.2	34.6	30.9	28.1	38.8	*b*
1,3-butadiene	28.9	33.0	33.4	27.2	24.1	26.0	*b*
1-butyne	35.6	32.7	33.5	30.4	28.4	39.5	*b*
2-butyne	24.4	21.1	21.8	18.4	16.4	34.7	*b*
but-1-yn-3-ene	65.0	65.7	66.5	62.8	59.8	72.8	*c*
butadiyne	102.2	102.2	103.3	100.3	97.2	113.0	*c*
cyclopropane	11.2	14.3	14.4	11.6	10.8	12.7	*b*
cyclopropene	68.2	68.7	69.3	67.2	65.7	66.2	*b*
cyclobutane	−11.9	−12.2	−12.1	−16.4	−17.5	6.8	*b*
cyclobutene	31.0	29.2	29.7	26.5	24.3	37.5	*d*
benzene	21.2	21.5	21.9			19.8	*b,l*
bicyclobutane	69.1	65.6	66.1	62.6	60.8	51.9	*b*
N_2	8.0	6.3	8.2	15.3	14.2	0.0	
NH_3	−6.3	−5.2	−5.1	−5.3	−5.4	−11.0	*e*
CH_3NH_2	−7.5	−4.1	−4.1	−5.5	−5.8	−5.5	*b*
$(CH_3)_2NH$	−6.6	−0.8	−0.8	−3.8	−4.4	−4.4	*b*
$(CH_3)_3N$	−2.8	4.9	5.0	3.3	2.4	−5.7	*b*
aziridine	25.2	34.0	34.3	32.1	31.2	30.2	*b*
pyridine	28.7	31.3	31.8			34.6	*b,l*
HCN	34.9	27.5	28.7	32.3	31.2	32.3	*e*
CH_3CN	18.9	11.1	12.5	13.3	11.7	20.9	*f*
$(CN)_2$	65.9	56.8	58.5	59.6	55.8	73.8	*b*
CH_3NC	60.0	35.9	36.4	35.9	34.5	35.6	*f*
N_2H_4	14.3	25.5	25.7	24.8	24.5	22.8	*e*
N_2H_2 trans	32.0	34.8	35.7	38.0	36.8	36	*g*
CH_2N_2	67.1	64.2	64.9	68.3	64.6	71	*h*
diazirine	72.5	79.9	81.5	83.0	80.7	79	*h*
HN_3	73.0	65.6	67.8	75.7	72.1	70.3	*f*
O_2	12.2	3.8	4.7	10.5	10.2	22.0	*i, j*
O_3	48.5	28.4	30.5	39.9	35.6	34.2	*e*
H_2O	−60.9	−60.0	−59.9	−59.7	−59.7	−57.8	*e*
CH_3OH	−57.4	−51.6	−51.6	−52.5	−52.7	−48.1	*b*
C_2H_5OH	−63.0	−57.7	57.6	−60.0	−60.5	−56.2	*b*
$(CH_3)_2O$	−51.2	−40.0	−39.9	−42.3	−42.9	−44.0	*b*
oxirane	−15.5	−5.3	−5.1	−6.6	−7.3	−12.6	*b*
H_2O_2	−38.2	−31.2	−31.0	−30.5	−30.7	−32.5	*e*
CO	−6.2	−29.4	−29.0	−25.6	−26.2	−26.4	*b*
CO_2	−75.4	−93.3	−92.8	−85.2	−86.8	−94.1	*b*
CH_2O	−33.0	−33.4	−33.1	−31.9	−32.5	−26.0	*b*
CH_3CHO	−42.4	−43.1	−42.7	−43.7	−44.8	−39.7	*b*
$(CH_3)_2CO$	−49.5	−50.7	−50.4	−52.8	−54.4	−51.9	*b*
CH_2CO	−7.0	−12.1	−11.7	−9.7	−11.6	−11.4	*k*
$(CHO)_2$	−61.6	−62.2	−61.8	−63.3	−65.7	−50.7	*b*
HCOOH	−92.7	−87.8	−87.5	−86.7	−87.7	−90.6	*b*
CH_3COOH	−101.2	−96.9	−96.6	−97.4	−98.9	−103.3	*b*
$HCOOCH_3$	−85.6	−74.2	−73.9	−75.1	−76.7	−83.6	*c*
N_2O	30.9	18.2	22.1	32.6	29.1	19.6	*e*
HONO trans	−40.6	−29.1	−28.7	−25.9	−27.6	−18.8	*e*
$HONO_2$	−17.5	−5.7	−4.7	0.0	−3.0	−32.1	*e*

[a] BWEN/SCF denotes BWEN calculation at the SCF optimized geometry (analogously DECI/SCF, CI/SCF). [b] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. [c] Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969. [d] Turner, R. B.; Goebel, P.; Mallon, B. J.; Doering, W. von E.; Coburn, J. F., Jr.; Pomerantz, M. *J. Am. Chem. Soc.* 1968, *90*, 4315. [e] Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.)* 1971, *NSRDS-NBS 37.* [f] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Baily, S. M.; Schumm, R. H. *NBS Tech. Note (U.S.)* 1968, *No. 270-3.* [g] Willis, C.; Lossing, F. P.; Back, R. A. *Can. J. Chem.* 1976, *54*, 1. [h] Benson, S. W.; Cruickshanck, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* 1969, *69*, 279. [i] Herzberg, G. "Spectra of Diatomic Molecules", 2nd ed.; Van Nostrand: New York, 1950. [j] Energy difference between the ${}^3\Sigma_g^-$ and ${}^1\Delta_g$ states: MNDO 18.3 kcal/mol, MNDOC 15.2 kcal/mol, exptl. 22.0 kcal/mol. [k] Nutall, R. L.; Lauffer, A. H.; Kilday, M. V. *J. Chem. Thermodyn.* 1971, *3*, 167. [l] No DECI, CI calculation due to the high number of configurations involved.

In general, the optimized parameters are rather similar in MNDOC and MNDO. The one-center energies U_{ss} and U_{pp} differ by less than 0.5 eV (except for U_{ss} of nitrogen). The orbital exponents ζ in MNDOC are consistently higher than those in MNDO, by 0.03–0.04 au. This is easily understood since electron correlation tends to increase bond lengths[34,36] which is compensated by higher orbital exponents. The MNDOC and MNDO resonance parameters β are again similar for the elements H, N, and O, whereas big changes are encountered for carbon. In the latter case, different β values are used for s and p electrons which allows for the fine tuning of the relative stability of saturated and unsaturated systems. Since electron correlation stabilizes unsaturated molecules more than saturated ones in MNDOC, the parametrization must produce a β_s/β_p ratio which is significantly different from the MNDO one. Finally, with regard to the repulsion parameters α, MNDOC and MNDO again show the same trends.

Results

In this section, we report MNDOC results for heats of formation and molecular geometries of a large number of compounds which have been selected to be representative of HCNO compounds. The molecules studied are a subset of the MNDO test molecules[37] including essentially all those with at most four nonhydrogen atoms. Larger molecules are mostly excluded to keep the computational effort at a reasonable level (see Computational Aspects).

Tables V and VI compare calculated and observed heats of formation for a set of 64 molecules. In our notation, the term "MNDOC results" without further specification refers to BWEN data at BWEN optimized geometries. For the purpose of comparison, Table VI also contains MNDO results[37] and MNDOC data from BWEN (eq 1), DECI (eq 2), and approximate CI (eq 3) calculations at SCF optimized geometries.

The statistical analysis (Table V) shows that MNDOC and MNDO are of similar quality with regard to the heats of formation of closed-shell ground-state molecules. The average absolute error is reduced from 6.2 kcal/mol in MNDO to 5.3 kcal/mol in MNDOC, but there is no consistent improvement of the results. Depending on the class of compounds studied, either one of the methods may be slightly superior. In both methods, the largest errors are encountered with four-membered rings, compounds with NO bonds, and sterically crowded molecules (e.g., neopentane which is too unstable by 15.7 kcal/mol in MNDO and by 14.8 kcal/mol in MNDOC). MNDOC and MNDO give slightly different results for three-membered rings, cyanides, alcohols, and ethers. However, in many cases, the trends of the results are fairly similar even for individual molecules (cf. Table VI).

MNDOC BWEN heats of formation at BWEN and SCF optimized geometries are very similar, the average absolute errors being 5.3 and 5.2 kcal/mol, respectively. For individual molecules, the discrepancies due to the use of different geometries rarely exceed a value of 1 kcal/mol (Table VI), which is far below the average absolute error of the method. This may be taken as a justification for using SCF optimized geometries in MNDOC studies, especially for larger molecules (cf. Computational Aspects).

After comparison of the performance of different correlation treatments at SCF optimized geometries, the following trends are found. On the average, the BWEN correlation energies differ by 11% from the DECI ones. For the molecules studied, this corresponds to a difference of typically 2–3 kcal/mol between MNDOC BWEN and MNDOC DECI heats of formation, saturated molecules usually being more stable in DECI and unsaturated ones in BWEN. The approximate CI correlation energies (Davidson correction, eq 3) are larger than the DECI ones by typically 6% (1–2 kcal/mol on an absolute scale). The average absolute errors in the calculated heats of formation are 5.2 (BWEN), 6.2 (DECI), and 6.5 kcal/mol (approximate CI). Since these values are of the same order of magnitude, it seems justified to carry out DECI or approximate CI calculations with unmodified MNDOC parameters (Table III), especially in cases where the simple BWEN approach is insufficient.

Table VII. Mean Absolute Errors for Optimized Bond Lengths and Bond Angles[a]

geometrical variable	N[b]	MNDO[c] SCF	MNDOC SCF	MNDOC BWEN
all bond lengths, Å	148	0.014	0.016	0.017
CH, Å	42	0.010	0.008	0.011
C–C, Å	29	0.012	0.011	0.013
C=C, Å	13	0.008	0.012	0.012
C≡C, Å	6	0.010	0.030	0.007
NH, Å	7	0.005	0.026	0.019
NC, Å	10	0.008	0.016	0.017
NN, Å	7	0.018	0.020	0.034
OH, Å	7	0.010	0.022	0.016
OC, Å	18	0.018	0.017	0.019
ON, Å	6	0.033	0.032	0.034
OO, Å	3	0.108	0.107	0.086
all bond angles, deg	71	2.9	2.8	2.6
HCH, deg	13	2.9	3.0	2.8
HCC, deg	15	1.6	1.4	1.4
CCC, deg	10	1.7	1.9	1.9
all angles at C, deg	48	2.0	2.0	1.9
all angles at N, deg	13	2.6	3.5	3.1
all angles at O, deg	10	7.1	5.3	4.8

[a] On the basis of the results in Table VIII. [b] Number of comparisons. [c] See footnote *c* of Table V.

Table VII shows a statistical comparison of MNDOC and MNDO results for bond lengths and bond angles. Table VIII contains optimized MNDOC structures for 59 molecules, at both the SCF and BWEN levels. Full structures are given for small molecules, but as a rule only the molecular skeletons are given for larger ones.

According to the statistical analysis (Table VII), the structural predictions by MNDOC and MNDO are of similar accuracy. MNDO seems to be slightly superior for bond lengths, with average absolute errors of 0.014 (MNDO) vs. 0.017 Å (MNDOC). In particular, the NH, NC, NN, and OH bond lengths are better reproduced by MNDO. On the other hand, bond angles are slightly more accurate in MNDOC, with average absolute errors of 2.9 (MNDO) vs. 2.6° (MNDOC); this applies especially to angles at oxygen.

With regard to individual molecules (Table VIII), we note that MNDOC predicts a C_2 structure for hydrogen peroxide (dihedral angle $\theta = 118.0°$), in agreement with experiment ($\theta = 119.1°$),[38] although the calculated trans barrier of 0.4 kcal/mol is somewhat too small (experimental value[39] 1.1 kcal/mol). In this case, the MNDO SCF optimization incorrectly predicts a C_{2h} trans minimum.[34,37]

In general, the MNDOC structures at the SCF and BWEN levels are rather similar. Some regular bond-specific trends are obvious (Table VIII): inclusion of electron correlation typically increases the lengths of single bonds by about 0.005 Å, of double bonds by about 0.020 Å, and of triple bonds by about 0.025 Å. Bond angles usually decrease by about 0.5° to produce more compact structures. These trends have also been found in exploratory calculations by using MNDO parameters,[34] indicating that they are not overly sensitive to the exact values of the parameters.

Discussion

A systematic comparison of MNDOC correlation energies (as obtained from eq 1–3) with ab initio correlation energies is not

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(34) Lauer, G.; Schulte, K.-W.; Schweig, A.; Thiel, W. *Theor. Chim. Acta* **1979**, *52*, 319.

(35) Weiner, P. K., Ph.D. Thesis, University of Texas, Austin, 1975.

(36) DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4085.

(37) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

(38) Khachkuruzov, G. A.; Przhevaliskii, I. N. *Opt. Spectrosc.* (*Engl. Transl.*) **1974**, *36*, 172.

(39) Hunt, R. H.; Leacock, R. A.; Peters, C. W.; Hecht, K. T. *J. Chem. Phys.* **1965**, *42*, 1931.

Table VIII. Molecular Geometries

molecule	point group	MNDOC SCF, BWEN (exptl) values for geometrical variables[a]	ref
H_2	$D_{\infty h}$	HH 0.655, 0.662 (0.742)	*b*
CH_4	T_d	CH 1.098, 1.104 (1.086)	*c*
C_2H_6	D_{3d}	CC 1.510, 1.512 (1.536); CH 1.104, 1.109 (1.091); HCC 111.3, 111.2 (110.9)	*b*
C_2H_4	D_{2h}	CC 1.318, 1.337 (1.339); CH 1.089, 1.092 (1.086); HCC 123.1, 123.0 (121.2)	*b*
C_2H_2	$D_{\infty h}$	CC 1.173, 1.198 (1.203); CH 1.058, 1.062 (1.060)	*b*
$CH_3CH_2CH_3$	C_{2v}	C^1C^2 1.520, 1.522 (1.526); C^1H^4 1.104, 1.109 (1.089); C^1H^5 1.104, 1.109 (1.094); C^2H^7 1.111, 1.116 (1.096); $C^1C^2C^3$ 115.7, 115.7 (112.4); $H^7C^2H^8$ 105.7, 105.6 (106.1); $H^4C^1C^2$ 110.3, 110.4 (111.8); $H^5C^1H^6$ 107.7, 107.7, (107.3); C^2–$C^1H^5H^6$ 129.2, 129.1 (126.4)	*b*, *h*
$CH_2{=}CHCH_3$	C_s	C^1C^2 1.326, 1.344 (1.336); C^2C^3 1.491, 1.494 (1.501); C^1H^4 1.089, 1.093 (1.081); C^1H^5 1.089, 1.092 (1.091); C^2H^6 1.096, 1.100 (1.090); C^3H^7 1.104, 1.109 (1.085); C^3H^8 1.105, 1.109 (1.098); $C^1C^2C^3$ 127.2, 126.9 (124.3); $H^4C^1C^2$ 122.2, 122.1 (121.5); $H^5C^1C^2$ 124.1, 124.0 (120.5); $H^6C^2C^1$ 118.9, 118.9 (119.0); $H^7C^3C^2$ 112.9, 112.8 (111.2); $H^8C^3H^9$ 107.7, 107.9 (106.2); C^2-$C^3H^8H^9$ 126.0, 126.0 (126.0)	*b*, *h*
$CH{\equiv}CCH_3$	C_{3v}	C^1C^2 1.177, 1.202 (1.206); C^2C^3 1.448, 1.450 (1.459); C^3H 1.105, 1.108 (1.105); C^1H 1.058, 1.061 (1.056); HC^3C^2 110.5, 110.3 (110.2)	*b*
$CH_2{=}C{=}CH_2$	D_{2d}	CC 1.294, 1.309 (1.308); CH 1.090, 1.093 (1.087); HCH 114.9, 115.2 (118.2)	*b*
n-butane	C_2	C^1C^2 1.521, 1.523 (1.533); C^2C^3 1.531, 1.533 (1.533); $C^1C^2C^3$ 115.1, 115.0 (112.4)	*b*
isobutane	C_{3v}	CC 1.533, 1.535 (1.525); CCC 112.4, 112.4 (111.2)	*b*
2-butene	C_{2h}	C^1C^2 1.491, 1.493 (1.508); C^2C^3 1.333, 1.351 (1.347); $C^1C^2C^3$ 126.5, 126.2 (123.8)	*b*
isobutene	C_{2v}	C^1C^2 1.335, 1.354 (1.330); C^2C^3 1.505, 1.506 (1.507); $C^1C^2C^3$ 121.8, 121.7 (122.4)	*b*
1,3-butadiene	C_{2h}	C^1C^2 1.329, 1.344 (1.341); C^2C^3 1.465, 1.461 (1.463); $C^1C^2C^3$ 125.8, 125.7 (123.3)	*b*
$CH_3C{\equiv}CCH_3$	D_{3d}	C^1C^2 1.447, 1.448 (1.467); C^2C^3 1.181, 1.204 (1.213); C^1H 1.105, 1.110 (1.115); HC^1C^2 110.5, 110.4 (110.7)	*b*
$CH{\equiv}CCH{=}CH_2$	C_s	C^1C^2 1.179, 1.199 (1.208); C^2C^3 1.423, 1.421 (1.431); C^3C^4 1.329, 1.345 (1.341); $C^2C^3C^4$ 125.1, 124.7 (123.1)	*b*
$CH{\equiv}CC{\equiv}CH$	$D_{\infty h}$	C^1C^2 1.179, 1.199 (1.205); C^2C^3 1.376, 1.368 (1.376); C^1H 1.058, 1.061 (1.046)	*b*
$CH_2{=}C{=}C{=}CH_2$	D_{2h}	C^1C^2 1.299, 1.315 (1.318); C^2C^3 1.261, 1.265 (1.283); C^1H 1.090, 1.093 (1.083)	*b*
cyclopropane	D_{3h}	CC 1.515, 1.521 (1.510); CH 1.095, 1.099 (1.089); HCH 110.8, 111.0 (115.1)	*b*
cyclopropene	C_{2v}	C^1C^2 1.315, 1.339 (1.296); C^1C^3 1.502, 1.512 (1.509); C^1H 1.070, 1.074 (1.072); C^3H 1.097, 1.100 (1.088); HC^1C^2 150.8, 150.4 (149.9); HC^3H 111.0, 111.5 (114.6)	*b*
cyclobutane	D_{2d}	CC 1.540, 1.544 (1.548); CH 1.102, 1.107 (1.133); HCH 107.3, 107.2 (108.1); $C^1C^2C^4C^3$ 180.0, 180.0 (153.0)	*b*
cyclobutene	C_{2v}	C^1C^2 1.342, 1.364 (1.342); C^1C^4 1.518, 1.522 (1.517); C^3C^4 1.557, 1.563 (1.566); C^1H 1.079, 1.083 (1.083); C^3H 1.102, 1.106 (1.094); HC^1C^2 135.5, 135.3 (133.5); HC^3H 108.0, 108.3 (109.2); C^1–C^4H_2 136.9, 136.8 (135.8)	*b*
benzene	D_{6h}	CC 1.398, 1.406 (1.397); CH 1.091, 1.094 (1.084)	*b*
bicyclobutane	C_{2v}	C^1C^2 1.515, 1.520 (1.498); C^1C^3 1.535, 1.570 (1.497); C^1H 1.080, 1.085 (1.071); C^2H_{eq} 1.097, 1.101 (1.093); C^2H_{ax} 1.097, 1.102 (1.093); $C^2C^3C^1C^4$ 123.3, 125.3 (121.7)	*b*
N_2	$D_{\infty h}$	NN 1.103, 1.136 (1.094)	*b*
NH_3	C_{3v}	NH 0.985, 0.993 (1.012); HNH 108.5, 107.6 (106.7)	
CH_3NH_2	C_s	CN 1.436, 1.444 (1.474); NH 0.986, 0.994 (1.011); HNC 113.2, 111.6 (112.0); HNH 109.2, 106.9 (105.9)	*b*
$(CH_3)_2NH$	C_s	CN 1.437, 1.442 (1.462); NH 0.986, 0.993 (1.019); CNC 120.9, 120.1 (112.2); HNC 113.3, 112.8 (108.9); H–NCC 143.3; 140.9 (125.4)	*b*
$(CH_3)_3N$	C_{3v}	CN 1.442, 1.445 (1.451); CNC 118.6, 118.6 (110.9)	*b*
aziridine	C_s	CN 1.464, 1.478 (1.475); CC 1.505, 1.519 (1.481); NH 0.989, 0.996 (1.016); H–NCC 121.4, 119.9 (112.5)	*d*
HCN	$C_{\infty v}$	CN 1.147, 1.176 (1.154); CH 1.067, 1.072 (1.063)	*b*
CH_3CN	C_{3v}	CN 1.150, 1.180 (1.157); CC 1.456, 1.459 (1.458); CH 1.104, 1.106 (1.104); HCC 110.0, 109.7 (109.5)	*b*
$(CN)_2$	$D_{\infty h}$	CN 1.149, 1.173 (1.154); CC 1.387, 1.382 (1.389)	*b*
CH_3NC	C_{3v}	C^1N^2 1.409, 1.414 (1.424); N^2C^3 1.178, 1.197 (1.166); C^1H 1.111, 1.114 (1.101); HC^1N^2 110.5, 110.4 (109.1)	*b*
H_2NNH_2	C_2	NN 1.393, 1.401 (1.449); NH 1.000, 1.007 (1.022); HNN 108.9, 108.5 (112.0); HNH 105.6, 105.0 (106.0); HNNH 180.0, 180.0 (90.0)	*b*
HNNH	C_{2h}	NN 1.218, 1.246 (1.252); NH 1.004, 1.009 (1.025); HNN 112.9, 111.8 (106.9)	*e*
CH_2N_2	C_{2v}	CN 1.286, 1.308 (1.32); NN 1.148, 1.163 (1.12); CH 1.091, 1.093 (1.08); HCH 119.6, 120.2 (127)	*b*
$HN^1N^2N^3$	C_s	N^1N^2 1.245, 1.244 (1.240); N^2N^3 1.132, 1.172 (1.134); N^1H 0.998, 1.003 (1.021); HN^1N^2 114.6, 115.1 (112.7); $N^1N^2N^3$ 165.9, 163.5 (180 ass)	*f*
O_2	$D_{\infty h}$	OO 1.135, 1.159 (1.216)	*b*
O_3	C_{2v}	OO 1.192, 1.221 (1.278); OOO 117.0, 117.0 (116.8)	*b*
H_2O	C_{2v}	OH 0.931, 0.936 (0.957); HOH 105.1, 104.6 (104.5)	*b*
H_2O_2	C_2	OO 1.298, 1.308 (1.452); OH 0.948, 0.954 (0.965); HOO 107.3, 107.5 (100.0); HOOH 129.2, 118.0 (119.1)	*g*

Table VIII (*Continued*)

molecule	point group	MNDOC SCF, BWEN (exptl) values for geometrical variables[a]	ref
CH_3OH	C_s	C^1O^2 1.375, 1.378 (1.425); C^1H^4 1.112, 1.117 (1.094); C^1H^5 1.116, 1.122 (1.094); O^2H^3 0.935, 0.941 (0.945); $C^1O^2H^3$ 109.6, 109.1 (108.5); $H^4C^1O^2$ 108.7, 108.6 (107.1); $H^5C^1H^6$ 106.8, 106.6 (108.6); O^2–$C^1H^5H^6$ 130.7, 131.0 (129.8)	*b*, *h*
$(CH_3)_2O$	C_{2v}	CO 1.382, 1.386 (1.410); COC 117.7, 117.2 (111.7)	*b*
oxirane	C_{2v}	CO 1.404, 1.413 (1.435); CC 1.500, 1.506 (1.470); CH 1.103, 1.108 (1.084); HCH 111.4, 111.3 (116.3); C–CH_2 158.4, 158.5 (158.1)	*b*
CO	$C_{\infty v}$	CO 1.144, 1.161 (1.128)	*b*
CO_2	$D_{\infty h}$	CO 1.176, 1.189 (1.162)	*b*
CH_2O	C_{2v}	CO 1.200, 1.213 (1.208); CH 1.110, 1.116 (1.116); HCH 111.9, 111.4 (116.5)	*b*
CH_3CHO	C_s	C^1C^2 1.513, 1.516 (1.501); C^2O 1.205, 1.221 (1.216); C^2H 1.117, 1.122 (1.114); C^1C^2O 125.9, 126.0 (123.9); C^1C^2H 112.8, 112.5 (117.5)	*b*
$(CH_3)_2CO$	C_{2v}	CC 1.526, 1.528 (1.507); CO 1.212, 1.226 (1.222); CCC 116.2, 115.9 (117.2)	*b*
CH_2CO	C_{2v}	CC 1.311, 1.325 (1.314); CO 1.173, 1.186 (1.161); CH 1.085, 1.088 (1.083); HCH 117.8, 118.5 (122.6)	*b*
CH≡CCH=O	C_s	C^1C^2 1.178, 1.197 (1.209); C^2C^3 1.448, 1.450 (1.445); C^3O 1.205, 1.216 (1.215); C^1H 1.060, 1.064 (1.055); C^3H 1.114, 1.114 (1.106); $C^1C^2C^3$ 178.8, 178.0 (178.4); C^2C^3O 124.6, 124.3 (123.6); C^2C^3H 112.2, 112.1 (113.9)	*b*
$(CHO)_2$	C_{2h}	CO 1.203, 1.214 (1.207); CC 1.532, 1.529 (1.525); CH 1.114, 1.122 (1.116); OCC 123.1, 123.5 (121.2); HCC 114.5, 114.1 (112.2)	*b*
HCO^1O^2H	C_s	CO^1 1.213, 1.226 (1.202); CO^2 1.344, 1.346 (1.343); O^2H 0.936, 0.944 (0.972); CH 1.115, 1.121 (1.097); O^1CO^2 122.7, 123.1 (124.9); HO^2C 113.8, 113.3 (106.3); HCO^1 125.5, 125.5 (124.1)	*b*, *h*
$CH_3CO^1O^2H$	C_s	CC 1.526, 1.531 (1.520); CO^1 1.218, 1.232 (1.214); CO^2 1.352, 1.351 (1.364); O^2H 0.936, 0.943 (0.970); CCO^1 125.9, 125.6 (126.6); CCO^2 114.0, 113.7 (110.6); CO^2H 113.3, 112.9 (107.0)	*b*, *h*
$HC^2O^1O^3C^4H_3$	C_s	O^1C^2 1.210, 1.222 (1.200); C^2O^3 1.351, 1.356 (1.334); O^3C^4 1.388, 1.393 (1.437); $O^1C^2O^3$ 124.3, 124.9 (125.9); $C^2O^3C^4$ 123.0, 122.3 (114.8)	*b*, *h*
N_2O	$C_{\infty v}$	NN 1.129, 1.180 (1.126); NO 1.175, 1.167 (1.186)	*b*
ONOH	C_s	NO^1 1.166, 1.180 (1.163); NO^2 1.316, 1.331 (1.433); O^2H 0.943, 0.947 (0.954); O^1NO^2 113.9, 113.9 (110.7); NO^2H 108.3, 108.1 (102.1)	*b*, *h*
O_2NOH	C_s	NO^1 1.204, 1.221 (1.199); NO^2 1.212, 1.223 (1.211); NO^3 1.350, 1.372 (1.406); O^3H 0.946, 0.952 (0.964); O^1NO^3 114.9, 114.4 (113.9); O^2NO^3 118.8, 119.0 (115.9); NO^3H 112.1, 111.1 (102.2)	*b*,*h*

[a] Bond length A^iB^j (in Å), bond angle $A^iB^jC^k$ (in deg), dihedral angle $A^iB^jC^kD^l$ (in deg) of A–B with respect to C–D measured counterclockwise along B–C, and angle A^i–$B^jC^kD^l$ (in deg) of A–B with plane BCD. The superscripts *i*, *j*, *k*, and *l* number the atoms in the molecule according to IUPAC rules; they are left out when the atoms can be specified unambiguously without them. [b] See Table VIII of ref 37. [c] Gray, D. L.; Robiette, A. G. *Mol. Phys.* 1979, *37*, 1901. [d] Bak, B.; Skaarup, S. *J. Mol. Struct.* 1971, *10*, 385. [e] Carlotti, M.; Johns, J. W. C.; Trombetti, A. *Can. J. Phys.* 1974, *52*, 340. [f] Amble, E.; Dailey, B. P. *J. Chem. Phys.* 1950, *18*, 1422. [g] Reference 38. [h] For the numbering of the atoms, see the structural formulas in Table VIII of ref 37.

Table IX. Bond Contributions (kcal/mol) to MNDOC Correlation Energies[a]

bond	BWEN	DECI	bond	BWEN	DECI
C–H	1.3886	1.5992	C=C	11.1388	11.7062
C–C	1.9502	2.8383	C≡C	17.4378	16.4856

[a] Calculated from the MNDOC results for CH_4, C_2H_6, C_2H_4, and C_2H_2 with the assumption of a constant C–H contribution.

possible due to the lack of published ab initio data. However, comparison for selected molecules[14,15,40] shows that the MNDOC correlation energies are typically 1 order of magnitude smaller than the ab initio ones. This discrepancy arises mainly from the smaller AO basis set and the integral approximations used in MNDOC.

Hence, the MNDOC correlation energy can in no way be regarded as an approximation to the "true" correlation energy defined as the difference between the energy at the Hartree–Fock limit and the exact nonrelativistic energy.[41] The MNDOC correlation energy rather is a model-specific quantity which accounts for part of the electron correlation that is not included via the semiempirical reduction of the two-electron integrals.

It would certainly be helpful if one could roughly estimate the MNDOC correlation energy of a particular molecule in advance. For this purpose, a bond additivity scheme seems feasible: Table IX contains contributions to the BWEN and DECI correlation energies from C—H, C—C, C=C, and C≡C bonds which have been calculated from the correlation energies of methane, ethane, ethylene, and acetylene. The MNDOC correlation energies can be estimated simply by adding these standard bond contributions. The discrepancies between these estimates and the actually computed correlation energies are fairly small: for the remaining 21 hydrocarbon molecules in Table VI, the average deviations are 8% for BWEN and 4% for DECI. On an absolute scale, this corresponds to an average of 2.0 kcal/mol for BWEN and 1.1 kcal/mol for DECI, appreciably below the average absolute errors in the MNDOC heats of formation. This demonstrates that the MNDOC correlation energies can approximately be partitioned into bond contributions.

The MNDOC correlation effects for closed-shell ground states are thus small, bond specific, and transferable between different molecules. This is exactly the situation where one would expect that such effects can, on the average, be well reproduced by a semiempirical parametrization at the SCF level. Therefore it is not surprising that MNDOC and MNDO are of similar accuracy for closed-shell ground states.

Hence, the remaining errors in the semiempirical treatment of closed-shell ground states are not primarily due to correlation effects. It may therefore be possible to remove these errors by improvements at the SCF level.

Conclusions

Electron correlation can be incorporated into semiempirical MNDO-type approaches in a consistent and efficient manner with use of second-order BWEN perturbation theory. The resulting MNDOC method can also be applied in conjunction with other correlation treatments (e.g., DECI) without modifying the

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(40) Pople, J. A.; Binkley, J. S. *Mol. Phys.* **1975**, *29*, 599.

(41) Löwdin, P.-O. *Adv. Chem. Phys.* **1959**, *2*, 207.

MNDOC parameters, as long as these treatments provide a reasonable approximation to the exact MNDOC correlation energy.

The explicit inclusion of electron correlation in MNDOC does not improve the calculated heats of formation and geometries of closed-shell ground states significantly, since the correlation effects in these systems can, on the average, be taken into account by a parametrization at the SCF level. Qualitative differences between MNDOC and MNDO can thus only be expected for systems which show specific correlation effects. This will be studied in the following two papers dealing with reactive species, transition states, and excited states.

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MNDOC Study of Reactive Intermediates and Transition States

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Abstract: MNDOC calculations on reactive species are carried out for methylene, cyclobutadiene, benzyne, and [18]annulene. Transition states of "allowed" thermal reactions are studied for the 1,2 hydrogen shift in vinylidene, the disrotatory ring opening of cyclopropyl cation, and the conrotatory ring opening of cyclobutene. The MNDOC correlation effects in these examples are discussed and compared with available ab initio results. MNDOC turns out to be superior to MNDO for systems which show specific correlation effects.

Experimental evidence about reactive intermediates and transition states is difficult to obtain. Theory may therefore provide valuable information concerning the detailed course of chemical reactions, and semiempirical methods have indeed been applied successfully to the study of chemical reactions.[1]

Reactive intermediates and transition states are often characterized by unusual bonding situations where electron correlation may be expected to play an important role. In these cases, there is some ambiguity in applying current semiempirical methods such as MINDO/3[2] or MNDO[3] which have been parametrized at the SCF level; usually either an SCF or a minimal CI treatment is carried out, the choice between them being made on an empirical basis.[4] The MNDOC[5] method, on the other hand, is free from such procedural problems since it has been parametrized to completely include correlation effects, within the framework of the MNDOC model.

To establish the reliability of MNDOC for the study of chemical reactions, it would be desirable to compile some statistical analysis similar to that for closed-shell ground states.[5] Unfortunately, this is not feasible due to the lack of accurate experimental data and the computational effort involved. In the present paper, we shall instead report on the MNDOC results for seven typical examples and discuss the correlation effects involved. The performance of MNDOC will be evaluated by comparisons with MNDO results, ab initio results, and experimental data (if available).

Theoretical Approach

Unless noted otherwise, MNDOC is applied in its standard version,[5] electron correlation being treated by second-order Brillouin–Wigner perturbation theory with Epstein–Nesbet energy denominators (BWEN). For the systems studied, one complication may arise which is not encountered with closed-shell ground states: if the energy of a particular doubly excited configuration Ψ_1 is only slightly above that of the SCF configuration Ψ_0, the corresponding contribution to the perturbation energy is overestimated since the energy denominator is very small (see eq 1 in ref 5). In this case, the lowest root of a 2 × 2 CI involving Ψ_0 and Ψ_1 must be taken as zero-order reference state in the perturbation treatment, the perturbation summation extending over all configurations which are doubly excited with respect to Ψ_0. This procedure is denoted by BWEN1.

If the two configurations Ψ_0 and Ψ_1 are degenerate or almost degenerate, the MNDOC correlation energy will also contain significant contributions from configurations corresponding to single or double excitations from Ψ_1 (i.e., including single, double, triple, and quadruple excitations from Ψ_0). A BWEN treatment using this configuration space and a zero-order state from a 2 × 2 CI will be termed BWEN2.

It should be emphasized that BWEN1 and BWEN2 do not represent any "special" correlation treatments. Our general philosophy[5] is to approximate the exact MNDOC correlation energy as closely and efficiently as possible. For ground-state singlets, this is achieved by a standard BWEN treatment with one main configuration, whereas a BWEN1 or BWEN2 treatment with two main configurations is required in the cases described above. Hence, BWEN1 and BWEN2 are simply the proper versions of perturbation theory if the two lowest configurations are close in energy.

In principle, BWEN2 should always be preferred over BWEN1 since it provides a better approximation to the exact MNDOC correlation energy. In practice, however, BWEN2 is considerably slower than BWEN1 due to the larger configuration space, whereas the results are fairly similar if the two relevant configurations are not too close in energy. In the present paper, we shall therefore adopt the following convention: BWEN2 will be used if the configurations Ψ_0 and Ψ_1 are separated by less than 1 eV, and BWEN1 in all other cases where Ψ_1 is considered to be important.

In our theoretical approach, there is one more choice to be made concerning the determination of the molecular orbitals (MOs): reactive intermediates and transition states are often open-shell species which might advantageously be described by open-shell

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(1) Dewar, M. J. S. *Chem. Br.* **1975**, *11*, 97.

(2) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

(3) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(4) Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 5650.

(5) Thiel, W. *J. Am. Chem. Soc.*, preceding paper in this issue.

0002-7863/81/1503-1420$01.25/0