MINDO/3: A Review of the Literature

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Contents

I. Introduction

The MINDO/3 technique, representing the third version of the Modified Intermediate Neglect of Differential Overlap method, is a semiempirical self-consistent-field (SCF) molecular-orbital (MO) approach to calculating electronic structures of molecules.[1,2] It has definite advantages over other MO calculations, including ab initio methods.[3,4] The strength of MINDO/3 lies in its ability to provide accurate values of molecular properties from relatively fast calculations on medium to large molecules (of up to 80 atoms) at about a fifth of the cost of ab initio methods. In fact, it has been stated[4] that MINDO/3 is more accurate than ab initio methods based on the Roothan–Hall approach[5,6] in obtaining agreement with experimental data and, additionally, MINDO/3 can execute MO calculations for larger molecules in a fraction of the time.

MINDO/3 is also a versatile method in that routines are included in the program[7,8] for MO calculations on ions and radicals of varying multiplicity, with or without the employment of configuration interaction (CI) techniques. There is also a facility for performing reaction-path calculations by using the reaction-coordinate routine. These useful inclusions coupled with the fact that input data is in the form of bond lengths and angles makes this program very attractive to the organic and medicinal chemist.

II. The MINDO/3 Method

MINDO/3 is an all-valence electron method and, as such, it is similar to Pople's NDO procedure[9] in that an approximation for the core Hamiltonian is retained and the valence electrons are assigned a minimum basis set of atomic orbital (AO) wave functions, ϕ_i. There is some equivalence to the INDO method as certain electronic repulsion integrals are neglected, but the modifications come in the way in which some of the remaining integrals are parametrized. Chart I summarizes the energy terms and their derivation as referred to in the Appendix.

Evaluation of the expectation value for the energy of the molecule involves derivation of the expression $\langle\phi|H|\phi\rangle$ where ϕ is the determinantal wave function.
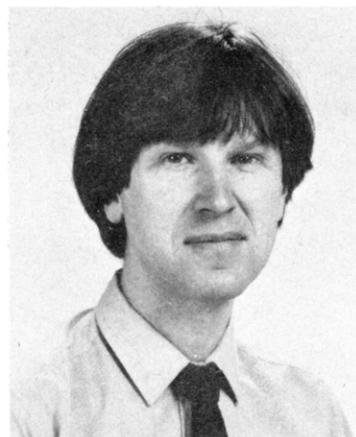
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The total Hamiltonian can be separated into one-electron and two-electron parts:

$$H = H_1 + H_2$$

where

$$H_1 = \sum_p H_{\text{core}(p)} \qquad H_{\text{core}(p)} = -\tfrac{1}{2}\nabla^2_{\text{p}} - \sum_A Z_A r_{pA}^{-1}$$

and

$$H_2 = \sum_{p<q}\sum r_{pq}^{-1}$$

In the MINDO/3 scheme certain adjustments and simplifying approximations are made in the treatment of the various one- and two-center integrals. These are as follows: (a) So that the calculations are invariant to rotation, all repulsion integrals (ii,jj) between AO i on atom m and AO j on atom n are made equal to a common value, γ_{mn}. (b) The 1-center repulsion integrals, g_{ik}, are left unchanged. (c) By use of the Goeppert–Mayer–Sklar potential function[10] which neglects penetration integrals

$$\int \phi_\rho(i)\frac{Z_s}{r_{si}}\phi_\rho(i)\,\mathrm{d}\tau_i$$

for electron–nuclear attractions, the attraction between an electron in AO i of atom m and core of atom n is given by

$$V_{in} = -C_n\gamma_{mn} \qquad (1)$$

where C_n is the core charge of atom n in units of the electronic charge.

CHART I

	Energy Term	Derivation
1-center integrals	coulombic attractions (n–e)	$U_{\rho\rho} = \int \phi_\rho(i) \left(-^1/_2 \nabla_i{}^2 - \frac{z_s}{r_{si}} \right) \phi_\rho(i)\ d\tau_i$
	interelectronic repulsions	$J_{\rho\rho} = \int\int \phi_\rho{}^*(i)\phi_\rho(i)\ \frac{1}{r_{ij}}\ \phi_\rho(j)\ d\tau_i$ $d\tau_j = \langle\rho\rho|\rho\rho\rangle$
	exchange terms	$K_{\rho\rho} = J_{\rho\rho}$
2-center integrals	electron-core attractions	$V_{\rho\sigma} = (-)\int \phi_\rho{}^*(i)\sum_s \frac{z_s}{r_{s\sigma}}\ \phi_\sigma(i)\ d\tau_i$
	resonance integrals	$R_{\rho\sigma} = \int \phi_\rho{}^*(i) \left(-^1/_2 \nabla^2 - \sum_s \frac{z_s}{r_{si}} \right) \phi_\sigma(i)\ d\tau_i$
	interelectronic repulsions	$J_{\rho\sigma} = \int\int \phi_\rho{}^*(i)\phi_\rho(i)\ \frac{1}{r_{ij}}\ \phi_\sigma{}^*(j)\phi_\sigma(j)$ $d\tau_i\ d\tau_j = \langle\rho\rho|\sigma\sigma\rangle$
	exchange integrals	$K_{\rho\sigma} = \int\int \phi_\rho{}^*(i)\phi_\sigma(i)\ \frac{1}{r_{ij}}\ \phi_\rho{}^*(j)\rho_\sigma(j)$ $d\tau_i\ d\tau_j = \langle\rho\sigma|\rho\sigma\rangle$
	core-core repulsions	$N = \sum_{s>t} \frac{z_s z_t}{R_{st}}$

The expression for the elements of the Fock matrix[11] in MINDO/3 is as follows:

$$F_{ii} = U_{ii} + 0.5q_i g_{ii} +$$
$$\sum_{j\neq i}^{(m)} q_j(g_{ij} - 0.5h_{ij}) - \sum_{n\neq m}^{(n)} \gamma_{mn}(c_n - \sum_j^{(n)} q_j) \quad (2)$$

where F_{ii} are the diagonal elements of the Fock matrix, U_{ii} is the sum of the KE of an electron in AO i of atom m and its PE due to attraction to the core of atom m, q_i is the electron population (density) of AO i, and g_{ij}, h_{ij} are the one-center coulomb and exchange integrals for AOs i and j, respectively.

$$F_{ij(mm)} = 0.5p_{ij}\ (3h_{ij} - g_{ij}) \quad (3)$$

$F_{ij\ (mn)}$ are the off-diagonal elements between AOs ij on atom m, and p_{ij} is the bond order between AOs i and j.

$$F_{ij(nm)} = \beta_{ij}{}^c - 0.5p_{ij} \quad (4)$$

where $F_{ij\ (mn)}$ are the off-diagonal elements between AOs i,j of different atoms m and n, and $\beta_{ij}{}^c$ is the two-center one-electron exchange integral (core-resonance integral).

The total energy of the molecule can be expressed as the sum of electronic and intercore repulsion energies as follows:

$$E_{\text{total}} = E_{\text{el}} + E_{\text{c}} + E_{\text{el}} + \sum_{m>n}\sum \text{CR}_{mn}$$

where CR_{mn} is the PE of repulsion between the cores of atoms m and n.

The energy of atomization (negative heat of formation) of any molecule is the difference in energy between that of the molecule and that of its constituent atoms. Atomic energies are calculated from single-configuration wave functions by using the same assumptions and integral values as in the MO calculations. Thus atomization energies can be equated with experimental heats of formation (Hf) values, where KE terms in Hf are taken into account in the parametrization. The parametrization in MINDO/3 takes into account and deals with the major sources of errors inherent in semiempirical NDO procedures: (1) neglect of coulombic electron correlation, (2) errors brought about by virtue of the simplifying assumptions made in the derivation, and (3) errors due to equating calculated atomization energies with measured heats of atomization.

In the original version of MINDO (1 and 2) the one-center integrals g_{ij} and h_{ij} were found from Slater–Condon parameters by Pople's method, as employed in INDO. MINDO/3, however, utilizes Oleari's method[12] whereby all the g_{ij} and h_{ij} integrals can be evaluated independently.

III. Optimization of Molecular Geometries

The geometry of a molecule is found by optimizing its total energy with respect to the corresponding geometric variables. In MINDO/3 input parameters are in the form of chemical bond lengths, bond angles, and dihedral or torsional angles. Thus the procedure is very chemist-oriented or chemist user friendly. Any number of these parameters may be optimized independently or grouped if desired, using the symmetry options. These allow one optimizable parameter to be linked to one or more other geometric parameters. This greatly facilitates convergence of the energy minimization procedure for optimization, decreasing the number of SCF calculations necessary, and hence diminishing computation time. There is also a facility for parameter dependence which invokes symmetry conditions. Thus, one optimizable parameter can be linked with another by a transformation operation, such as rotation through a specified angle. For example, a nitro (NO_2) group can be rotated relative to, say, a benzene ring by optimizing the dihedral angle of one of the NO_2 oxygen atoms relative to a benzene ring carbon atom, while stipulating that the other oxygen atom of the nitro group remains in the same plane of rotation.

Obviously, the larger the molecule, the more time it takes to optimize a large number of parameters, though it is possible to optimize all the geometric parameters for small molecules (of about 10 atoms) with a relatively fast rate of convergence. For medium-sized molecules (of about 40 atoms) it is advisable to optimize about five parameters simultaneously, otherwise a lengthy oscillating iterative procedure ensues which can be misleading (or erroneous) in the final result by producing a local minimum, instead of the global minimum of total energy.

Generally, it is best to start with reliable crystal data, microwave data, or (at the worst) tabulated values of standard bond length, bond angles, and dihedral angles as input geometric parameters. Any parameters that

TABLE I. Ionization Energies for DNA Bases, eV[a]

	expt	MINDO/3	CNDO	SCF
adenine	8.00	7.60	10.08	7.92
cytosine	8.90	8.70	10.78	8.16
thymine	9.43	9.31		8.80
guanine	7.80	7.66	9.06	7.59

[a] Data from ref 195.

TABLE II. Dipole Moments for Monosubstituted Benzenes, Debyes[a]

compd	calcd	expt
PhF	1.62	1.60
PhCl	1.69	1.69
$PhNH_2$	1.00	1.13
$PhNO_2$	4.88	4.28
PhOH	1.41	1.45
PhOMe	1.31	1.30
PhCOMe	3.26	3.02

[a] Data from ref 195.

are either not available, or not known to any great certainty, can be optimized by the geometry minimization techniques.

IV. Critical Assessment of MINDO/3

MINDO/3 has been criticized for having certain shortcomings brought about the parametrization methods employed. It is true that for chemical bonds containing a substantial degree of d orbital character, such as those involving sulfur or phosphorus, discrepancies occur in the calculation. Such errors are inevitable and, in fact, no parametrization exists in MINDO/3 for S=O and P=O bonds, though amendments can be made to the program to include them.

MINDO/3 has a propensity for overestimating torsional (dihedral) angles between singly bonded sp[2] atom centers. This is because the Davidon–Fletcher–Powell (DFP) minimization procedure[13,14,15] does not have an adequate weighting to allow for the stability of coplanar π-systems.

However, other semiempirical methods suffer from the same shortcomings and, if accurate molecular geometries are known from X-ray crystallographic data, little or no optimization is necessary. It has been found that changes in torsional angles have the least effect on electron densities, whereas these and other calculated electronic structural parameters are more susceptible to changes in bond lengths and angles. MINDO/3 correctly predicts the position of a hydrogen atom in a carboxylic acid ($-CO_2H$) group as lying coplanar with the carbonyl moiety. The rotation of a methyl ($-CH_3$) group adjacent to an aromatic ring system is correctly optimized at 60° to the plane of the ring, and the preferred conformations of biomolecules such as histamine and serotonin are in agreement with accepted conformational studies by other techniques. Also the C–O–C bond angles in ethers and esters, as estimated by MINDO/3, are close to the tabulated values. A slight overestimation of C–H, O–H, and N–H bond lengths has been found using this method, though not greater than by other methods, but this problem can be overcome if literature values are employed, and little optimization is necessary.

It has been said that MINDO/3 gives inaccurate orbital energies, which may be true, but it is difficult to verify or disprove because of the lack of experimental data. The energies of the highest occupied MOs (HOMOs) are equivalent to first ionization energies of molecules, and these compare favorably with experimental values. Results for DNA bases (Table I) show that MINDO/3 estimates ionization energies better than other MO methods. Dewar has compared MINDO/3 calculated molecular properties with those calculated by other methods demonstrating that MINDO/3 is better than even ab initio calculations.[16] Jorgensen and Salem used MINDO/2 calculated orbital energies together with ab initio values to list orbital

energies for a large number of small molecules.[17] McManus et al.[18,19] have criticized MINDO/3 in displaying systematic errors in the calculation of heats of formation of alkanes and cycloalkanes. However, Dewar has answered many of the criticisms to MINDO/3 and MNDO by showing their advantages to other MO methods.[4]

MINDO/3 can exaggerate dipole moments if considerable geometry optimization is employed, but if crystal data or microwave data are input for geometric parameters, very good agreement with experimental values can be achieved, as shown in Table II. Clearly MINDO/3 is as good a method for electronic structure calculation as any other available. It would appear to fill the gap between CNDO, IEHT, and ab initio methods, and it has several advantages over all of these. MINDO/3 can produce accurate results on a vast range of molecules at comparably low cost in terms of computer time. The following survey shows that MINDO/3 is still holding its own against supposedly better MO methods 10 years after its inception.

V. MINDO/3 Calculations on Molecules of Biological and Chemical Interest

The early literature concerning the utilization of MINDO methods has been reviewed by Murrell and Harget,[20] Klopman and Evans,[21] and Fernandez-Alonso,[22] who stress the usefulness of MINDO in application to a wide range of studies in theoretical chemistry and biochemistry, e.g., excited states, photochemical reactions, insertion reactions, catalysis, and enzymic reactions. Tables III–VII summarize the use of MINDO/3 in different chemical, physicochemical, and biological situations.

Dewar and Ramsden first published results based on MINDO/3 calculations in 1973[23] together with NDDO studies on three-membered ring systems. This new version of MINDO/3 was an improvement on its predecessors MINDO[24] and MINDO/2[25] written by the Dewar group of co-workers. Over the next three years, Dewar and his group demonstrated the applicability of MINDO/3 to a whole range of compounds, intermediates, and reactions of essentially chemical interest by the publication of a plethora of papers.[1-3,26-52] In 1974, these workers reported MINDO/3 studies on bisdehydrobenzenes,[26] rearrangements of cyclobutadiene dimers,[27] chemiluminescence,[28] dioxetane,[29] Diels–Alder reactions,[30] conversion of cyclobutene to 1,3-butadiene,[32] [18]annulene,[34] and nonbenzenoid aromatic systems.[2] Their contributions to theoretical chemistry involved applications of MINDO/3 in the additivity of bond energies[31] and the calculation of molecular electric polarizabilities.[33] The following year showed activity by

TABLE III

structural parameters	molecules considered	ref	structural parameters	molecules considered	ref
electronic structure	antiaromatic 3-membered rings	23	electronic structure	phenol and methyl phenols	205
electronic structure	bisdehydrobenzenes	26	electronic structure	$(CH)_8{}^{2+}$ structures	209
electronic structure	[18]annulene	34	electronic structure	alkylpyridines and N-methylpyridinium ions	225
electronic structure	non-benzenoid aromatics	2			
electronic structure	cations	40	electronic structure	dioxetane	234
electronic structure	cyclobutadiene	42	electronic structure	bicyclo[6.2.0]decapentaene	231
electronic structure	methylene, nitrene, and oxygen	47	electronic structure	arylenamines	243
electronic structure	oxazoles and imidazoles	50	electronic structure	2-nitrobenzimidazoles	245
electronic structure	organic radicals	59	electronic structure	N-nitroenamines	246
electronic structure	nonclassical ins	73	electronic structure	enamines and dienophiles	248
electronic structure	tropylium ions and benzyl cations	74	ground states	hydrocarbons	1, 35
electronic structure	1,3-dipoles	82	ground states	C, H, O, and N species	36, 37
electronic structure	$C_7H_7O^+$ ions	87	ground states	molecules containing 3rd-row elements	38
electronic structure	propyl cations	91			
electronic structure	7-norbornyl cations	100	rotational barriers	ethane, cyclic ketones, isobutyleneacetone	57
electronic structure	carbonyl oxides	102			
electronic structure	chlorocarbenes	106	orbital interactions	monohomoaromatic molecules	61
electronic structure	$C_2H_6{}^+$ and $C_2H_4X^+$ X = H, F, Cl, CH_3	107	molecular geometry	para-substituted anilines	83
			molecular geometry	strained hydrocarbons	154
electronic structure	nitrenium ions	108, 194	molecular geometry	naphthalene ions	171
electronic structure	tricyclo[4.1.0.0]hept-3-enes	119	molecular geometry	phosphines	181
electronic structure	chlorobutatriene and chlorobuteynes	120	hydrogen bonding	water, acetaldehyde, ammonium, methanol, and carboxylic acid dimers	97, 98, 199
electronic structure	C_8H_9 cation and its congeners	145			
electronic structure	strained polycyclic hydrocarbons	146	charge distributions	27 molecules. (furan, pyrrole, quinol, etc.)	112
electronic structure	nitrobenzene	147			
electronic structure	succimimido radical	156	P–C bond parameterization	phosphoorganic compounds	122
electronic structure	small molecules	161			
electronic structure	hydrocarbon ions	162	P–C bond parameterization	open-shell systems	129
electronic structure	1st row MH_2 and MH_3 hydrides	166, 167			
electronic structure	monocyclic compounds	168	P–O, P–Cl, and P–F bond parameterization	organophosphorus compounds	170
electronic structure	organophosphorus compounds	169			
electronic structure	methoxynitroanilines	172	conformational analysis	conjugated systems	135
electronic structure	amides, ureas, and hetercycles	174	geometry optimization	pyrimidine bases	150
electronic structure	alkenes and chloroalkanes	177	cone angles	phosphorus ligands	155
electronic structure	tetraatomic clusters	179	molecular conformation	tertiary immonium ions	160
electronic structure	eight-membered conjugated carbocycles	185	molecular conformation	N_2O_6	188
			molecular conformation	triaminoguadinium ion	210
electronic structure	catalytic surface structures	187	molecular inversion	trivalent nitrogen compounds	164
electronic structure	cycloalkenylcarbenes	197	cyclic models	solid and surface structures	220
electronic structure	cyclooctatetraenes	198	inductive effect	compounds containing heteroatoms	244
electronic structure	iron hydrides, oxides, and $Fe(CO)_5$	200			
electronic structure	saturated alicyclics containing Cl, N, O, S	201	binding energy	diamond and graphite	249

the same group with further studies on hydrocarbons,[35] carbon compounds with other elements,[36,37] third row elements,[38] cations,[40] cyclobutadiene,[42] reactive carbene and nitrene intermediates and oxygen,[47] oxazoles and imidazoles.[50] Reactions and rearrangements of bicyclobutane,[41] methyl bicyclo[2.1.0]pent-2-enes,[44] Dewar benzene,[46] vinyl cyclopropane,[49] and the reactions between singlet oxygen and carbon–carbon double bonds[45] were reported in the same year by Dewar and his colleagues at Austin University. In the sphere of physical chemistry they also published MINDO/3 calculations of ionization potentials of radicals,[39] ESCA chemical shifts,[43] nitrogen-14 nuclear quadrupole coupling constants,[48] hyperpolarizabilities of fluoromethanes,[51] and optical coefficients of lithium formate.[52] The latter two papers appearing in 1976 after Dewar's reply[53] to criticisms of MINDO/3 which had been made by Pople[54] and Hehre[55] in the previous year. Dewar has summarized the usefulness of MINDO/3 as a theoretical experimental procedure of great value in a very readable article in ref 16 in 1975, and the attractiveness of MINDO/3 prompted its use by other groups of workers.

Graczyk et al. used MINDO/3 in the evaluation of C–Cl stretching vibrational force constants of *tert*-butyl chloride in the same year,[56] and in 1976 MINDO/3 was employed in calculations of rotational barriers by

Combs and Rossie,[57] reaction pathways for the reaction between atomic carbon and ethylene oxide (Figuera et al.),[58] electronic structure of radicals by Bischof,[59] the vinylcyclopropane rearrangement by Andrews and Baldwin,[60] orbital interactions in aromaticity (Jorgensen),[61] and on anomalous energy minima (Combs and Rossie).[62]

Encouraged by their earlier successes and eager to spread confidence in MINDO/3, the Dewar group published further work in 1977. They studied a number of molecular arrangements of chemical interest such as the rearrangement of benzyl, toluene, and cycloheptatriene ions,[63,64] the Cope[65,66] and Conforth rearrangements,[67] the rearrangements of substituted benzyl cations,[68] and the rearrangements of phenylcarbene to cycloheptatriene.[69] Other reactions subjected to MINDO/3 investigations were the addition of singlet oxygen to 1,3-butadiene,[70] the thermal decarboxylation of but-3-enoic acid,[71] and hydrogen elimination from organic cations.[72] Related to some of these studies was further work on non-classical ions,[73] monosubstituted tropylium ions, and benzyl cations.[74] They also investigated molecular properties relating to spectroscopic and other physico-chemical data, such as vibrational frequencies,[75] NMR coupling constants,[76] force constants,[77] heat capacities and entropies,[78] and applied

TABLE IV

physicochemical parameters	molecules considered	ref
bond energies	11 hydrocarbons	31
electric polarizabilities	21 small molecules	33
ionization potentials	organic radicals	39
ionization potentials	phosphines	123
ionization potentials	P_2X_4	136
ionization potentials	imines and diimines	206
hyperpolarizabilities	fluoromethanes	51
nonlinear optical coefficients	lithium formate	52
anomalous energy minima	various molecules	62
heat capacities and entropies	27 small molecules (H_2O, C_6H_6, etc.)	78
dipole moments	12 small molecules (H_2O, HCN, etc.)	85
potential energy surface	$C_3H_5^+$ and $C_3H_3^+$	105
molecular dissociation	hydrogen	121
force field calculations	small molecules	130
dipole moment derivatives	10 small molecules (H_2O, HCN, etc.)	131
electron affinities	maleic anhydride and its derivatives	152
atom-in-molecule polarizabilities	electron-donor/acceptor molecules	178
atom-in-molecule polarizabilities	8 small molecules (H_2O, CH_4, C_6H_6, etc.)	158
magnetic susceptibilities	6 small molecules	153
ionization energies	organic radicals	159
nitration rates	explosives	165
enthalpies of formation	organic and organometallic peroxides	183
heats of formation	carbocations	202
heats of formation	neutral and ionic hydrocarbons	203
heats of formation	H_2O_3 and H_2O_4	223
enthalpies of atomization	200 organic molecules	204
potential energy surface	$C_9H_9^+$	215
chemisorption on graphite	H_2 and electrophilic adsorbates	216, 217, 218
partition coefficients	various molecules	255
isotope effects	CH_3OH, CH_3NH_2, CH_3SH, and deutero analogues	132, 138
isotopic exchange equilibria	8 small molecules (CH_4, H_2O, NH_3, etc.)	157
reduced partition function ratios	various molecules and deutero analogues	219, 239, 241

TABLE V

spectroscopic parameters	molecules considered	ref
ESCA chemical shifts	45 small molecules (C, N, and O)	43
^{14}N NQR coupling constants	N_2, NH_3, HCN, HN_3, nitriles pyridine, pyrazine	48
NMR coupling constants	57 small molecules (eg, H_2O, C_2H_6, C_6H_6)	76
C–Cl stretching vibration	*tert*-butyl chloride	56
vibrational frequencies	34 small molecules (eg, H_2O, C_2H_6, C_6H_6)	75
vibrational frequencies	C_2H_4, H_2O, CH_3NH_2, and deutero analogues	77
vibrational frequencies	cyclobutadiene	79
vibrational frequencies	molecules containing 3rd row heteroatoms	237
C–N spin–spin coupling constants	HCN, CH_3NC, CH_3NH_2, CH_3NO_2, pyridine	90
nuclear spin–spin coupling constants	20 small molecules	124
C and N screening constants	32 small molecules (eg, CO, CO_2, C_6H_6, N_2)	133
B and F chemical shifts	20 BR_3 compounds, 23 F compounds	134
hyperfine coupling constants	small organic radicals	137
harmonic force constants	9 small molecules and radicals	139

MINDO/3 calculated vibration frequencies to cyclobutadiene.[79] Dewar and Thiel[80,81] also introduced a new

NDO procedure (similar to MINDO/3) called MNDO which supposedly gave better results in MO calculations of electronic structure.

In 1977 other groups of workers used MINDO/3 in MO calculations for molecules of biological and chemical interest. Caramella et al. used MINDO/2 and MINDO/3 in geometry optimization of molecules in order to derive the shapes and energies of molecular orbitals,[82] and Parr and Wasylishen studied the planarity of the amino group in para-substituted anilines.[83] Jennings and Worley outlined a concerted rotation-pyramidalization pathway in a study of C=N bond rotation in methyleneamine N-oxide,[84] derivatives of dipole moments were reported by Pandey et al.,[85] and McManus and Worley evaluated the importance of carbocation solvation in halonium ion–carbocation equilibria.[86] Dits et al. looked at $C_7H_7O^+$ ions using MINDO/3,[87] Kyba used MNDO and MINDO/3 to study hydrogen shifts to an alkylcarbene center,[88] whereas Boyd calculated the electronic structure of β-lactams.[89] Schulman applied MINDO/3 in the calculation of C–N spin–spin coupling constants,[90] Al-Khowaiter and Wellington performed MINDO/3 calculations on some carbonium ions,[91] and Fleischhauer demonstrated the application to MINDO/3 in the study of ground-state reactions.[92] The number and variety of uses that MINDO/3 had been put to demonstrated that it was fast becoming a successful theoretical technique in chemistry.

During the next year, the Dewar group made a smaller contribution to the literature on MINDO/3, possibly due to their involvement with MNDO.[93] However, they pursued their interest in reaction mechanisms by MINDO/3 studies on the Norrish Type II reaction of butanal,[94] the retro-Diels–Alder reaction of cyclohexene,[95] and some radical addition reactions.[96] Dewar also collaborated with Klopman et al. in a study of hydrogen bonding using MINDO/3.[97] Although the latter showed the apparent inability of the method to find energy minima in two hydrogen-bonded system, the study was by no means exhaustive and, therefore, inconclusive.

Zielinski et al. also studied hydrogen-bonded systems using MINDO/3.[98] Their results also cast doubts on the use of this method in predicting energy minima, though they may have encountered local minima instead of global minima in their calculations. In spite of these and other criticisms[18,99] MINDO/3 had wide application in 1978. Studies on unstable species and reaction intermediates were particularly in evidence.

Furusaki and Matsumo[100] performed MINDO/3 calculations on norbornyl cations, Lechtken looked at the thermolysis of 1,2-dioxetanes,[101] Hull calculated the stability of Craigee carbonyl oxides,[102] Beatty et al. investigated cyclic chloronium ions,[103] Bodor and Pearlman studied the dihydropyridines,[104] and Krause et al. used MINDO/3 for evaluating potential energy surfaces of an ion fragmentation reaction.[105] In the same year, Lee and Rothstein elucidated the electronic structures of chlorocarbene intermediates,[106] Lischka and Koehler investigated the structure and stability of carbocations in comparison with ab initio methods,[107] Bonicamp executed MINDO/3 calculations on nitrenes,[108] Olah et al. studied onium ions using MINDO/3,[109] Kahlil employed MINDO/3 in reaction-path

TABLE VI

chemical reactions	molecules considered	ref	chemical reactions	molecules considered	ref
kinetic effects	pyridine and its derivatives	184	hydrogen insertion	cyclopropenylidene and cyclopropylidene	230
pericyclic reactions	Dewar benzene	28	steroidal ring closure	olefins	113
thermolysis	dioxetane	29	spin-forbidden reactions	$^1O_2$, $^3O_2$, and C_2H_2	114
thermolysis	bicyclobutane	41	acid-catalyzed ring opening	oxaziridine	116
thermal conversion	cyclobutene	32	meta and para methylation	substituted catechols	127
Diels–Alder reaction	1,3-butadiene and C_2H_4	30	β-elimination potential surface	ethylene and hydrochloric acid	140
thermal isomerization	bicyclo[2.1.0]pent-2-enes	44	elimination reaction	nitroethane	141
reaction with C=C bonds	$^1O_2$ and simple alkenes	45	elimination reaction	ethanol and ethanethiol	142
electrocyclic conversion	Dewar benzene	46	elimination reaction	chloroalkanes	148
rearrangement	vinyl cyclopropane	49, 60	nucleophilic substitution	5-coordinate group V and VI (group 5 and 6)^a compounds	143
rearrangement	benzyl cation	63			
rearrangement	toluene and cycloheptatriene	64	nucleophilic substitution	furan and its derivatives	144
Cope rearrangement	1,5-hexadiene and its derivatives	65, 66, 115, 251	reaction-pathway calculation	methane and methyl cation	176
molecular rearrangement	alkylcarbene	88	thermal rearrangement	cyclopentadienes	27
molecular rearrangement	C_4H_7 radicals	128	thermal rearrangement	bicyclobutanylidene	182
molecular rearrangement	substituted benzyl cations	68	addition reaction	free radicals	180
molecular rearrangement	phenylcarbene	69	heterolysis reaction	neopentyl alcohol	186
molecular rearrangement	methyleneamine N-oxide	84	Menschutkin reaction	alkylpyridines	196
reduction of atomic carbon	ethylene oxide	58	1,3-sigmatropic shifts	odd electron ions	207
Cornforth rearrangement	5-methoxyoxazole-4-carboxamide	67	photochemical mechanism	methylenamine N-oxide	208
addition of $^1O_2$	1,3-butadiene	70	thermal electrocyclic reaction	chromenes	211
thermal decarboxylation	but-3-enoic acid	71	fragmentation reaction	protonated acetates	212
solvation and rearrangement	halonium cations and carbocations	86	noncatalytic epoxidation	olefines	213
ground-state reactions	various molecules	92	reaction mechanism	azabicyclic compounds	221
Norrish type II reaction	butanol	94	insertion reaction	cyclopentadienylidene	222
retro-Diels–Alder reaction	cyclohexane	95	Meyer–Schuster rearrangement	α-acetylenic alcohols	224
radical-addition reaction	methyl radicals, simple alkenes, C_2H_2	96	mechanism of formation	carbinolamines	227
ion fragmentation	carbon–carbon biradical, phenyl cation	101, 175	reduction	pyridinoid heterocycles	228
ion fragmentation	doubly charged benzene	189	cheletropic reactions	4-cyclopentenone + N-(3-pyrrolinyl)nitrene	229
ionic rearrangement	cyclic chloronium ion/chloroalkyl ion	103	reduction of CO	acetylenediolate anion	232
protonation reaction	dihydropyridines	104	tautomerism	2-hydroxypyrrole + its derivatives	233
protonation reaction	onium ions of NH_2OH, Me_2SO, and acetone oxime	109	dehydrochlorination	1,1,2-trichloroethane	242
			hetero-Diels–Alder reaction	acrylaldehyde/ethene + butadiene/methanol	247
reaction pathway	protonted alkanes	238	chemical reactivity	perfluoroalkenes	226
reaction pathway	methane anion	110	chemical reactivity	ionol	252
reaction pathway	methane and F^-	117	sigmatropic rearrangements	systems with central carbon atom	250
hydrogen elimination	organic cations	72	reaction with dienophiles	α-(dimethylamino)styrene	253
hydrogen migration	methyl carbene	111	reaction with O_2	ethene	254
hydrogen addition	vinylidene	163			

^{a} In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III → 3 and 13.)

calculations on methane anions[110] and Martin utilized MINDO/3 in calculating the excited states of methyl carbene.[111] Also, Wellington and Al-Khowaiter reported work on the charge distributions in a number of molecules and ions.[112] Other reactions studied using MINDO/3 in the same year include ring closure in olefinic cyclization,[113] interaction of molecular oxygen with acetylene,[114] the Cope rearrangement,[115] the acid-catalyzed ring opening of oxaziridine,[116] and the reaction between methane and the fluoride ion.[117] Bischof et al. published papers on bicyclic and tricyclic compounds,[118,119] Zuccarello and co-workers calculated the molecular structures of chlorobutatriene and chlorobutenynes,[120] whereas Fleischhauer et al. studied the dissociation of hydrogen using MINDO/3.[121] After parametrization of the P–C bond, Goetz et al. obtained structural data for organophosphorus compounds.[122,123] MINDO/3 was also used in the calculation of nuclear spin–spin coupling constants.[124] Finally, biological ap-

plications of MINDO/2 and MINDO/3 were made by various authors in 1978. Zielinski et al. employed MINDO/2 in geometry calculations of DNA bases,[125] Worley and co-workers investigated the electronic structures of biological piperazines,[126] and Shinagawa reported MINDO/3 studies on meta and para methylation of substituted catechols by catechol O-methyl transferase.[127]

From 1979 onward, the output of MINDO/3 publications by the Dewar group has been considerably diminished with respect to their earlier activity. However, while allowing other groups of workers to explore the uses of MINDO/3, Dewar and his colleagues continued to employ the method in exploring molecular properties. In 1979 Dewar and Olivella reported a MINDO/3 study of rearrangements of butyl radicals,[128] and compared MINDO/3 with other MO methods for calculating the energies and geometries of open shell systems.[129] Others have used MINDO/3 in the computation of physical

TABLE VII

biological activity	molecules considered	ref
antibacterial	N-substituted monocyclic β-lactams	89
antimicrobial	piperazines	126
carcinogenicity	aromatic hydrocarbon epoxides	149
N-hydroxylation by P-450	amines	151
P-450 oxidation pathways	methane and ethylene	173
NADH-type reductions	cyclopropenium cation	190
NADH-type reductions	3-carbamoylpyridimium cation	191
coenzyme activity	oxidized flavins	192
inhibition of aniline hydroxylation and P-450 binding	alcohols	193
QSARs, antitumoractivity	phenylaziridines, aniline mustards, nitrosoureas	195
P-450 oxidation reactions	CCl$_4$ and CHCl$_3$	236
enzyme specificity	P-450 and P-448 substrates	256, 257
P-450 spin-state equilibria	alkylbenzenes	258
QSARs, biological activity	benzoxazoles, resorufins, coumarins, methylene dioxy benzenes, polyaromatic hydrocarbons, polychlorobiphenyls, and phthalate esters	259, 260

parameters. Silvi performed molecular force field calculations,[130] Wolinski and Sadlej investigated the reliability of MINDO/3 in calculation of dipole moments,[131] Koehler used MNDO and MINDO/3 to calculate secondary isotope effects,[132] whereas Jallali-Heravi and Webb estimated carbon and nitrogen screening constants[133] and also boron and fluorine chemical shifts.[134] Dodziuk found shortcomings in MINDO/3 when applied to conformational analysis of conjugated systems,[135] though Frenking et al. utilized MINDO/3 in conformational calculations of organophosphorus compounds.[136] Pandey and Chandra studied isotropic hyperfine coupling constants in radicals by MINDO/3,[137] Engel and co-workers investigated isotope effects,[138] and Al-Jiburi et al. used MINDO/3 in the calculation of force constants and vibrational frequencies and intensities in vibrational spectra of organic molecules.[139]

In the physicochemical area, MINDO/3 found employment in transition-state studies[140,141,142] by Faustov et al., whereas Minyaev and Minkin and Pronin et al. investigated nucleophilic substitution reactions using MINDO/3.[143,144] Chemical studies in the same year included a study by Jefford and co-workers of the bridged C$_8$H$_9$ cation,[145] Favini et al. looked at the molecular structure of strained polycyclic hydrocarbons,[146] Davis and Guidry calculated the electronic structure of nitrobenzene,[147] whereas Faustov and Yufit studied the effect of substituents on the activation energy of chloroalkane dehydrohalogenation.[148] Finally in 1979, biological applications of MINDO/3 were initiated by Klopman et al. who calculated the conformations of benzo(a)pyrene epoxides and related this to their carcinogenicity,[149] Czerminski and co-workers reported MINDO/3 calculations on some pyrimidine bases,[150] and Pack and Loew used MINDO/3 and MNDO in studies of the mechanism of N-hydroxylation of amines by cytochrome P-450.[151]

The literature regarding MINDO/3 in the 80s reflects a continuation of its use in established areas such as reactive intermediates and transition states, calculation

of electronic structural properties for a wide variety of compounds, and an increase in its application to biological molecules.

In 1980, MINDO/3 was employed in calculating physicochemical parameters, and in investigating physicochemical systems. Fleischhauer and Asaad determined electron affinities of maleic acid derivatives,[152] Pandey and Chandra studied magnetic susceptibilities of small molecules using MINDO/3,[153] Maksic et al. compared ab initio methods with MINDO/3 in calculating interatomic distances in hydrocarbons.[154] De-Santo and co-workers utilized MINDO/3 to calculate phosphorus ligand cone angles,[155] Kikuchi et al. predicted the π and σ electronic states of the succinimido radical,[156] Boeck et al. used MNDO and MINDO/3 calculations in a study of isotropic exchange equilibria,[157] Metzger evaluated polarizabilities using INDO and MINDO/3,[158] and Nakajima et al. estimated radical ionization energies by MINDO/3 as an aid to the interpretation of mass spectra.[159] Lelj et al. investigated the conformation of and hydrogen migration in some tertiary immonium ions by MINDO/3,[160] Tapia and Silvi reported a MINDO/3 study of solvent effects on the structure and properties of simple molecules,[161] Khalil performed MINDO/3 calculations on some hydrocarbon ions,[162] Chiu and Li studied the addition of hydrogen to vinylidine by the same method,[163] Jennings and Worley applied MNDO and MINDO/3 to trivalent nitrogen inversions,[164] and Andoh et al. showed that MINDO/3 could be used in estimation of nitration rates by the Hammett rule.[165]

Chemical studies using MINDO/3 in 1980 included calculations by Glidewell and Bews on first row hydrides,[166,167] Felker et al. looked at monocyclic structures,[168] Frenking and co-workers published MNDO and MINDO/3 work on organophosphorus compounds,[169,170] Sycheva and Zakharov reported MINDO/3 calculations on naphthalene ions,[171] and Buemi et al. studied methoxynitroanilines by MINDO/3 and INDO/S.[172] Application of MINDO/3 to reactions and molecules of biological interest was apparent in 1980. Pudzianowski and Loew studied cytochrome P-450 hydrocarbon oxidation mechanisms by looking at hydroxylation and epoxidation pathways for methane and ethylene,[173] whereas Defina and Andrews used MINDO/3 to investigate the electronic structure of amides, ureas, and some heterocycles.[174] These co-workers showed that MINDO/3 could be applied to heteroatomic molecules with a good degree of confidence.

In 1981 the volume of literature regarding MINDO/3 was somewhat reduced, though there was an increase in biological studies. Chemical and physicochemical applications of MINDO/3 continued to be in evidence. Tasaka et al. performed a MINDO/3 study on the fragmentation of the phenyl cation,[175] Pronin and Holer investigated the mechanism of the gas-phase equilibrium between methane and the methyl cation,[176] van Hemelrijk et al. calculated the molecular structures of alkenes and chloroalkanes using MINDO/3,[177] Metzger estimated molecular polarizabilities using MINDO/-FP,[178] Cuthbertson and Glidewell studied some tetraatomic clusters,[179] and Koehler and Knoll calculated activation of entropies of free-radical addition reactions.[180] In the same year Mosbo et al. performed MINDO/3 calculations on phosphines,[181] Chiu and Li

reported a MINDO/3 study of thermal rearrangements on bicyclobutanylidine,[182] Kokorev et al. calculated the electronic structures of organic and organometallic peroxides,[183] Seeman and co-workers correlated kinetic effects with MINDO/3-derived geometries,[184] Huang et al. studied conjugated eight-membered carbocycles,[185] Ando et al. calculated kinetic isotope effects in the heterolysis of neopentyl alcohol using MINDO/3,[186] Pel'menshchiov et al. investigated catalytic surface structures by the same method,[187] Gloriozov and co-workers reported MINDO/3 calculations of the conformations of N_2O_6,[188] and Bentley and Wellington published details of the electronic structures of doubly charged benzene and its isomeric dications.[189]

MINDO/3 calculations on molecules of biological interest included a study of reduced NAD by Donkersloot and Buck,[190,191] Teitell reported a study of oxidized flavins,[192] Testa investigated the electronic and structural factors which influence the inhibition of aniline hydroxylation by alcohols and their binding to cytochrome P-450,[193] Ford and Scribner published details regarding MNDO calculations of nitrenes derived from carcinogenic aromatic amines and amides,[194] and Lewis showed that MINDO/3 could be used to generate QSARs for tumor-inhibitory phenyl aziridines, aniline mustards, and nitrosoureas, DNA bases, and carcinogenic polycyclic hydrocarbons.[195] Here it was shown that MINDO/3 could be modified to include calculations of superdelocalizabilities, molecular electrostatic potential energies, and could be parametrized for the C–S and S=O bonds.

In the next year, the number of MINDO/3 publications was diminished. Chemical applications of the method were pursued by Viers et al. who investigated iodomethylation of alkylpyridines,[196] Kansch and Duerr performed EHT, CNDO/2, and MINDO/3 calculations on cycloalkenylcarbenes,[197] Mak and Li studied some cyclooctatetraenes,[198] Mohammed and Hopfinger looked at hydrogen bonding by using CNDO/2 and MINDO/3,[199] and Blyholder et al. applied a version of MINDO/3 to explore semiempirical calculations on transition-metal compounds.[200]

Physical chemical parameters were estimated using MINDO/3 in 1982. McManus et al. evaluated the geometry optimization capability of MINDO/3,[201] Harris et al. calculated carbocation heats of formation,[202] Kuehnel and co-workers reported MINDO/3 calculations of hydrocarbon heats of formation,[203] Shlyapochnikov et al. obtained atomization enthalpies,[204] Eckert-Maksic studied the protonation of phenols,[205] Frost et al. compared MINDO/3 with other semiempirical methods in the estimation of ionization potentials of imines,[206] and Hoppilliard and Bouchoux calculated barriers to 1,3-sigmatropic shifts in odd electron ions.[207] Kikuchi and co-workers carried out a MINDO/3 study involving CI of the mechanism for the photochemical reaction of methylenamine N-oxide to oxaziridine,[208] Klumpp et al. investigated some $(CH)_3^{2+}$ structures,[209] Bracuti and Carignan calculated the conformation of the triaminoguadinium ion,[210] Simkin and co-workers studied the course of thermal electrocyclic reactions of chromenes,[211] Shigihara et al. looked at the fragmentation of protonated acetates,[212] and Kokorev et al. calculated the electronic structures of peroxides by using MINDO/3.[213]

There was an increase in MINDO/3 publications in 1983. Physical applications included conformational studies on acyclic tetrasulfides by Askari and Karimian,[214] Huang et al. calculated the potential energy surfaces of the $C_9H_9^+$ ion,[215] and Illas et al. looked at the chemisorption of hydrogen on graphite[216] and at the chemisorption of electrophilic adsorbates on graphite.[217] The chemisorption of hydrogen on graphite was further investigated by Casanas,[218] Hanschmann calculated reduced partition function ratios of isotopically substituted molecules,[219] and Zakharov and Litinskii reported a program for calculating cyclic models of solid and surface structures by using MINDO/3.[220]

Physicochemical parameters were estimated by MINDO/3 calculations in 1983. Schmidt et al. showed that photoelectron spectra could be compared with MINDO/3 in the study of the mode of reaction of azabicyclic compounds,[221] Tsang and Li looked at the reaction between molecular hydrogen and cyclopentadienylidene,[222] Khadzhi-Ogly et al. estimated heats for formation of hydrogen peroxide homologues,[223] and Andres et al. studied the intramolecular solvolytic mechanism of the Meyer–Schuster reaction.[224]

A number of chemical applications of MINDO/3 appeared in 1983. Seeman and co-workers derived molecular geometries and energies of alkylpyridines and their cations,[225] Gey et al. studied the reactivity of perfluoroalkenes,[226] Shokhen et al. looked at the reaction mechanism of carbinolamine formation,[227] Budzelaar and colleagues applied MINDO/3 to the reduction of pyridine heterocyclics[228] while Dewar and Chantranupong studied some cheletropic and reverse Diels–Alder reactions.[229] Tsang and Li continued their MINDO/3 investigations in published work on hydrogen insertions of cyclopropenylidene and cyclopropylidene,[230] Spanget-Larsen calculated the structure of bicyclo[6.2.0]decapentaene,[231] Santiago et al. reported a MINDO/3 study on the monoelectronic reduction of carbon monoxide,[232] and Ribo and Valles looked at the tautomerism of 2-hydroxypyrrole.[233]

Biological applications of MINDO/3 and MNDO in 1983 included a MINDO/3 study of dioxetanone, a postulated intermediate involved in chemiluminescence and bioluminescence, by Kasney et al.,[234] whereas Shea et al. used MNDO in the calculation of kinetic isotope effects in model cytochrome P-450 oxidations.[235] Their results indicated that P-450 mediated O-dealkylation and carbon oxidation proceed via hydrogen abstraction by triplet "oxene-like" species, though this does not occur for N-dealkylation. In the same year, Pudzianowski, Loew, and others reported an MO study of model cytochrome P-450 oxidation of CCl_4 and $CHCl_3$.[236] MNDO calculations showed that triplet oxygen interacts with these halothanes by two mechanisms. In the oxidative metabolism of CCl_4 initial transformation of trichloromethyl hypochlorite occurs, which then loses electrophilic chlorine to form the hypochlorite and then decomposes into phosgene, an observed in vitro product. The metabolism of $CHCl_3$, however, involves hydroxylation to trichloromethanol which then forms phosgene without loss of electrophilic chlorine.

MINDO/3 investigations continued to be reported in 1984. A number of studies involved the estimation of physical and physicochemical parameters. Al-Jibury et al. calculated vibration frequencies and absorption

intensities of a number of molecules using the MIN-DO/3–FORCES method,[237] Planelles and co-workers utilized a large protonated alkanes reaction surface model as a test for the accuracy of MINDO/3,[238] and Hanschmann reported further work on partition function isotopic ratios for hydrogen,[239] carbon,[240] and oxygen and nitrogen isotopes.[241] Bolotin et al. published an investigation of the catalytic dehydrochlorination of 1,1,2-trichloroethane,[242] Koikov et al. performed electronic structural calculations on arylenamines,[243] and Gineityte and Shatkovskaya used MINDO/3 to describe the inductive effect of heteroatoms.[244]

Chemical and biochemical applications of MINDO/3 were also carried out in the same year. Lopyrev et al. performed calculations on 2-nitrobenzimidazoles,[245] Ivshin and co-workers elucidated the structures of N-nitro enamines,[246] Lee et al. undertook a MINDO/3 study of the hetero-Diels–Alder reaction,[247] Koikov et al. also looked at reactions of enamines with dienophiles using MINDO/3,[248] Ricart and co-workers executed MINDO/3 calculations on periodic systems,[249] Cho et al. determined the reactivity of certain molecules involved in sigmatropic hydrogen rearrangements,[250] Slanina reported a further study of the Cope rearrangement,[251] and Luzhkov and Isichenko applied INDO, MINDO/3, and molecular electrostatic potential-energy calculations to the reactivity of ionol.[252] The Koikov group in the Soviet Union also compared MINDO/3 calculations with experimental data for the reaction of α-dimethylaminostyrene with dienophiles.[253] With biochemical oxygen insertions in mind, Minaev and Tikhomirov published work on the mechanism of the reaction between molecular dioxygen and ethylene.[254]

The literature over the past 10 years shows an evolving interest in MINDO/3 calculations which reflect the particular strengths of the method in its application to molecular systems which would be difficult to study by other MO methods. At the time of writing MINDO/3's use in 1985 cannot be described with completeness. However, Klopman published estimations of partition coefficients for a large number of molecules using MINDO/3 and HMO methods of calculation, with the employment of quantitative structure–property relationships from MO data,[255] and Lewis et al. have applied MINDO/3 calculations in order to produce computer-graphic representations of molecular dimensions for a large number of substrates of cytochromes P-450 and P-448.[256,257] Here it has been established that, essentially, there are two groups of substrates which exhibit specificity for the two groups of enzymes. This specificity is determined by the structural requirements of the binding sites of the two types of cytochromes, so that thin relatively planar molecules bind preferentially to and activate cytochromes P-448 which causes the production of toxic metabolites, whereas ellipsoidal molecules bind to and activate cytochromes P-450, which brings about detoxification. A number of further papers by Lewis et al. on similar work have been submitted to various journals with expected publication in 1986. These are QSAR studies of cytochromes P-450 substrates, including alkyl benzenes,[258] alcohols, polycyclic aromatic hydrocarbons, aliphatic amines, alkoxy resorufins, methylene dioxybenzenes, and coumarins.[259] Other MINDO/3-gener-

ated QSAR work has been performed on β-blocking aryloxypropanolamines, polychlorobiphenyls, antiinflammatory benzoxazoles, monosubstituted benzenes, and clofibrate analogues and phthalate esters.[260]

The literature shows that MINDO/3 has been successfully applied to the calculation of electronic structures of an enormous variety of medium-sized molecules, giving rise to accurate values of many physical and theoretical parameters. The MINDO/3 method of MO calculation readily lends itself to the investigation of chemical reactions, and to problems of biological interest, due to its ease of use, its relative speed and consequently its low cost. It is also adaptable to modification in order to include calculation of molecular electrostatic potentials, superdelocalizabilities, and the structures of second-row elements. Although the Dewar group are currently working on a new and improved version of MINDO/3, I imagine that it will still be extensively used in the future for fast, accurate, calculations of electronic structural parameters.

VI. Appendix

Derivation of Molecular Properties for Molecular Orbital Methods. For molecules it is valid to describe the energy, E, of any electronic state in terms of the Hamiltonian operator, H, and the wave function, ψ, by $H\psi = E\psi$ (the eigenvalue equation) where $H = T(\text{KE}) + V(\text{PE})$. The expectation value (mean value) of E is given by

$$E = \int \frac{\psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

where ψ^* is the complex conjugate of ψ and $d\tau$ indicates that the integration is over all space or, simply, by using Dirac's notation

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

The total energy of the molecule can be treated as the sum of electronic energy, E_{el}, and internuclear repulsion energy E_{nucl}. The latter is given by

$$E_{nucl} = \sum_{\mu\nu} \frac{Z_\mu Z_\nu}{R_{\mu\nu}}$$

where $Z_{\mu,\nu}$ are charges on nuclei μ,ν of internuclear distance $R_{\mu\nu}$. Electronic energy is the sum of all KE terms, electron–nucleus attractions, interelectronic repulsions, and interelectronic exchange terms. This can be written as

$$E_{el} = \sum_i H_i + \sum_{i<j} J_{ij} - \sum_{i<j} K_{ij}$$

where H_i is the one-center core Hamiltonian given by:

$$H_i = \int \phi_i^* H^c \phi_i \, d\tau_i$$

$$H^c = -\tfrac{1}{2} \underset{\text{KE}}{\sum_i \nabla_i^2} - \underset{\substack{\text{electron–}\\ \text{nuclear attraction}}}{\sum_{\mu,i} \frac{Z_\mu}{r_{\mu i}}}$$

∇^2 is the del^2 operator =

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

J_{ij} is the electron–electron repulsion integral:

$$J_{ij} = \int \int \phi^*_1(i)\phi_1(i)\frac{1}{r_{ij}}\phi^*_2(j)\phi_2(j) \ d\tau_i \ d\tau_j$$

K_{ij} is the interelectron exchange integral:

$$K_{ij} = \int \int \phi^*_1(i)\phi_2(i)\frac{1}{r_{ij}}\phi^*_1(j) \ \phi_2(j) \ d\tau_i \ d\tau_j$$

The total energy may thus be written

$$E_{\text{tot}} = \sum_1 H_i + \sum_{i<j}(J_{ij} - K_{ij}) + \sum_{\mu<\nu}\frac{Z_\mu Z_\nu}{R_{\mu\nu}}$$

Dealing with the H_i term, we first use the LCAO formalism for describing the MOs $\psi_\nu(i)$ in terms of the basis set of aos $\phi_\rho(i)$ as follows:

$$\psi_\nu(i) = [\sum_\rho c_{\nu\rho}\phi_\rho(i)]\sigma_\nu(i)$$

where $\sigma_\nu(i)$ is the spin factor (α or β). Then

$$H_i = \int \psi_\nu(i)\left(-\nabla_i^2 - \sum_r \frac{Z_r}{r_{ri}}\right)\psi_\nu(i) \ d\tau_i$$

$$= \int_\rho c_{\nu\rho}\phi_\rho(i)$$

$$\left(-\tfrac{1}{2}\nabla_i^2 - \sum_r \frac{Z_r}{r_{ri}}\right)\sum_\sigma c_{\nu\sigma}\phi_\sigma(i) \ d\tau_i \int \sigma_\nu^2(i) \ d\sigma_i$$

But

$$\int \sigma_\nu^2(i) \ d\sigma_i = 1$$

and therefore, we get

$$H_i = \sum_\rho \sum_\sigma c_{\nu\rho}c_{\nu\sigma} \int \phi_\rho(i)\left(-\tfrac{1}{2}\nabla_i^2 - \sum_r \frac{Z_r}{r_{ri}}\right)\phi_\sigma(i) \ d\tau_i$$

These integrals may now be classified as follows in two types:

(1)

$$H_{\rho\rho} = \int \int \phi_\rho(i)\left(-\tfrac{1}{2}\nabla_i^2 - \frac{Z_r}{r_{ri}}\right)\phi_\rho(i) \ d\tau_i \int \phi_\rho(i) \times$$

$$\left(-\sum_{s\neq r}\frac{Z_s}{r_{si}}\right)\phi_\rho(i) \ d\tau_i$$

where the second term is the sum of the penetration integrals $P_{\rho s}$ representing the attraction of nuclei s for the charge distribution represented by ϕ_ρ^2 (centered on nucleus r). These terms are small and often neglected in semiempirical methods. The first term in $H_{\rho\rho}$ is an atomic integral, which is usually assumed to have the same value as in the free atom.

(2) $\qquad H_{\rho\sigma} = \int \phi_\rho(i)\left(-\tfrac{1}{2}\nabla^2 - \sum_r \frac{Z_r}{r_{ri}}\right)\phi_\sigma(i) \ d\tau_i$

If ρ and σ are centered on the same atom, $H_{\rho\sigma} = 0$. Otherwise, $H_{\rho\sigma}$ is the resonance integral and is a measure of covalent bonding.

Treatment of J_{ij} gives us

$$J_{\mu\nu} = \int \int \sum_\rho c_{\mu\rho}\phi_\rho(i)\sum_\sigma c_{\nu\sigma}\phi_\sigma(j)$$

$$\frac{1}{r_{ij}}\sum_\tau c_{\mu\tau}(i)\sum_\nu c_\mu\phi_\nu(j) \ d\tau_i \ d\tau_j \int \sigma_\mu^2(i)\sigma_\nu^2(j) \ d\sigma$$

TABLE VIII

$\int \phi_\rho\phi_\sigma d\tau$	overlap integral
$\int \phi_\rho(i)\left(-\tfrac{1}{2}\nabla^2 - \sum_s \frac{Z_s}{r_{si}}\right)\phi_\rho(i)d\tau_i = H_{\rho\rho}$	core Hamiltonian
$\int \phi_\rho(i)h(i)\phi_\sigma(i) \ d\tau_i = H_{\rho\sigma}$	resonance integral
$\int \phi_\rho(i)\frac{Z_s}{r_{si}}\phi_\rho(i) \ d\tau_i = H_{\rho s}$	penetration integral
$\langle \rho\rho\|\rho\rho\rangle = \Gamma_{\rho}\rho$	one-center coulombic repulsion integral
$\langle \rho\rho\|\sigma\sigma\rangle = \Gamma_{\rho\sigma}$	two-center coulombic repulsion integral
$\langle \rho\sigma\|\rho\sigma\rangle$	exchange integral
$\langle \rho\rho\|\rho\sigma\rangle$	hybrid integral
$\langle \rho\sigma\|\rho\tau\rangle, \ \langle \rho\rho\|\sigma\tau\rangle$	three-center integrals
$\langle \rho\sigma\|\tau\nu\rangle$ etc. (8 in all)	four-center integrals

Since the spins integrate to unity, rearrangement gives that

$$J_{\mu\nu} =$$

$$\sum_\rho\sum_\sigma\sum_\tau\sum_\nu c_{\mu\rho}c_{\nu\sigma}c_{\mu\tau}c_\nu \int \int \phi_\rho(i)\phi_\sigma(j)\frac{1}{r_{ij}}\phi_\tau(i)\phi_\nu(j) \ d\tau_i \ d\tau_j$$

For 1-center integrals, $\Gamma_{\rho\rho}$, $\rho = \sigma = \tau = \nu$, such that

$$\Gamma_{\rho\rho} = \int \int \phi_\rho^2(i)\phi_\rho^2(j)\frac{1}{r_{ij}} \ d\tau_i \ d\tau_j$$

If $\rho = \tau$ and $\sigma = \nu$, but $\rho \neq \sigma$, we get the coulombic repulsion integral, $\Gamma_{\rho\sigma}$, where

$$\Gamma_{\rho\sigma} = \int \int \sigma_\rho^2(i)\phi_\sigma^2(j) \ d\tau_i \ d\tau_j$$

which may involve two centers if ρ and σ are on different atoms, or one center if they are on the same atom. When $\rho = \sigma$, $\tau = \nu$, we get the exchange integral given by:

$$\int \int \phi_\rho(i)\phi_\sigma(j)\frac{1}{r_{ij}}\phi_\rho(j)\phi_\sigma(i) \ d\tau_i \ d\tau_j$$

which may be one- or two-center. A shortened form of this utilizes the bra–ket notation of Dirac, i.e.,

$$\Gamma_{\rho\rho} = \langle \rho\rho\|\rho\rho\rangle$$

$$\Gamma_{\rho\rho} = \langle \rho\rho\|\rho\rho\rangle$$

Table VIII summarizes the type of integrals required in a rigorous MO treatment.

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