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Appendix

Calculation of Energy $E_3{}^i$ for Excited States Based on the Antisymmetric Product of Two Isolated Molecular Wave Functions. The single configuration wave function for an excited state corresponding to an electron excitation from MO α to MO μ ($\phi_\alpha \rightarrow \phi_\mu$) is described as

$$\begin{aligned} {}^{1,3}\Phi = {} & (1/\sqrt{2})[\{\phi_1(1)\bar{\phi}_1(2)\ldots\phi_{n-1}(2n-3)\bar{\phi}_{n-1}(2n-2) \times \\ & \phi_\alpha(2n-1)\bar{\phi}_\mu(2n)\} \pm \{\phi_1(1)\bar{\phi}_1(2)\ldots\phi_{n-1}(2n-3) \times \\ & \bar{\phi}_{n-1}(2n-2)\phi_\mu(2n-1)\bar{\phi}_\alpha(2n)\} \equiv \\ & (1/\sqrt{2})[\{\ldots.\alpha\bar{\mu}\} \pm \{\ldots.\mu\bar{\alpha}\}] \end{aligned} \tag{A-1}$$

where $\{\ \ \}$ is a Slater determinant and $\phi_1, \ldots, \phi_{n-1}$ are assumed not to include ϕ_α or ϕ_μ. The plus and minus signs correspond to the singlet and triplet, respectively.

We assume MO's are normalized but not orthogonal. The nonorthogonal form is rather inconvenient for the energy calculation. By any orthogonalization technique such as the Schmidt method, one can mutually orthogonalize (and renormalize) doubly occupied MO's ϕ_1 to ϕ_{n-1} without changing the total wave function ${}^{1,3}\Phi$ except for the unimportant normalization constant. Let us assume this has been done. The orthonormalization of ϕ_α to the now orthonormal $\phi_1, \phi_2, \ldots, \phi_{n-1}$ does not change the total wave function. The orthonormalization of ϕ_μ to $\phi_1, \phi_2, \ldots, \phi_{n-1}$ does not change the total wave function either. Let us assume that these orthonormalizations have been completed and that $\phi_1, \phi_2, \ldots, \phi_{n-1}, \phi_\alpha$, and ϕ_μ describe resultant MO's. Now let us orthonormalize the new ϕ_μ to the new ϕ_α by using

$$\phi_\mu{}' = (\phi_\mu - S_{\alpha\mu}\phi_\alpha)/(1 - S_{\alpha\mu}{}^2)^{1/2} \tag{A-2}$$

where $S_{\alpha\mu}$ is the overlap integral between ϕ_μ and ϕ_α. The total wave function is then

$$\begin{aligned} {}^{1,3}\Phi = {} & \sqrt{2}S_{\alpha\mu}\{\ldots\alpha\bar{\alpha}\} + (1/\sqrt{2}) \times \\ & (1 - S_{\alpha\mu}{}^2)^{1/2}[\{\ldots.\alpha\bar{\mu}'\} \pm \{\ldots.\mu'\bar{\alpha}\}] \end{aligned} \tag{A-3}$$

which is not normalized. The energy associated with this is written as

$$\begin{aligned} {}^{1,3}E = {} & [\{{}^2_0\}S_{\alpha\mu}\{E(\ldots.\alpha\bar{\alpha})S_{\alpha\mu} + 2(1 - S_{\alpha\mu}{}^2)^{1/2} \times \\ & \langle\ldots.\alpha\bar{\alpha}|H|\ldots..\alpha\bar{\mu}'\rangle\} + (1 - S_{\alpha\mu}{}^2)\{E(\ldots.\alpha\bar{\mu}') \pm \\ & K_{\alpha\mu}{}'\}]/(1 + S_{\alpha\mu}{}^2)^{1/2} \end{aligned} \tag{A-4}$$

In the EHP method the common MO's can be used for both the ground and excited states.[7] Therefore, $E(\ldots.\alpha\bar{\alpha})$ is the ground state energy E^{G}. $E(\ldots.\alpha\bar{\mu}') \pm K_{\alpha\mu}{}'$ can be replaced by the excitation energy ${}^{1,3}\Delta E(\alpha \rightarrow \mu')$ plus the ground state energy E^{G}. $\langle\ldots..\alpha\bar{\alpha}|H|\ldots.\alpha\bar{\mu}'\rangle$ is replaced by $\sqrt{2}F_{\alpha\mu}{}'$, where $F_{\alpha\mu}{}'$ is the matrix element of the Hartree–Fock operator between MO α and μ'.

Thus the energies for the singlet and triplet states ${}^{1,3}\Phi(\alpha \rightarrow \mu)$ are, respectively

$${}^3E = E^{\mathrm{G}} + {}^3\Delta E(\alpha \rightarrow \mu') \tag{A-5}$$

$$\begin{aligned} {}^1E = E^{\mathrm{G}} + {} & [(1 - S_{\alpha\mu}{}^2)\,{}^1\Delta E(\alpha \rightarrow \mu') + \\ & 2\sqrt{2}S_{\alpha\mu}(1 - S_{\alpha\mu}{}^2)^{1/2}F_{\alpha\mu}{}']/(1 + S_{\alpha\mu}{}^2) \end{aligned} \tag{A-6}$$

The above described procedure was followed for the actual calculation of the energy associated with $\Phi_0{}^{\mathrm{F}_i} \cdot \Phi_0{}^{\mathrm{W}_0}$.

Semiempirical Molecular Orbital Calculations and Molecular Energies. A New Formula for the β Parameter

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Contribution from the Department of Chemistry, St. Louis University, St. Louis, Missouri 63156. *Received April 23, 1973*

Abstract: A new expression for the core Hamiltonian integral H_{ab} over symmetrically orthogonalized orbitals is derived for semiempirical MO methods, based on the commutator equation $[\mathbf{r},h] = \mathbf{p}$. Implementation of this formula leads to a theoretically satisfactory improvement for the INDO method. The formula is parameterized so as to duplicate the binding energies of homonuclear diatomic molecules. Calculations on a large number of first row diatomics and triatomics show a marked improvement for bond energies and force constants and even some improvement of the good dipole moments and bond distances of the original INDO method.

Despite recent advances in computer technology, rigorous solution of the Roothaan-SCF equations is still not generally feasible for polyatomic molecules. The principal problem in *ab initio* calculations is the large number of difficult integrals over basis functions that are required. The last decade has seen the introduction of a number of semiempirical all-valence electron SCF methods. Rather than actually evaluate all the integrals needed, these methods neglect many of the integrals altogether and take values for many of the

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others either from experimental data or as empirical parameters. Once this has been done, the orbitals are iteratively determined so as to minimize the energy, exactly as in an *ab initio* calculation.

The success of such a method obviously depends on the manner in which the different integrals are approximated. Perhaps no other integral has received so much attention as the off-diagonal core Hamiltonian integral.

$$H_{ab} \equiv \langle\phi_a| - {}^1/_2\nabla^2 - \sum_A Z_A/r_A|\phi_b\rangle$$

ϕ_a and ϕ_b are basis functions and the summation is over all nuclei. The great majority of the approximations employed for H_{ab} are based on some more or less complicated proportionality to the overlap integral S_{ab}.

$$H_{ab} = fS_{ab} \tag{1}$$

f is either a constant or a function of other parameters. Expressions of type 1 are invariant with respect to a rotation of the coordinate system of the molecule and have been shown to work quite well in semiempirical π electron methods. There is an additional complicating factor in an all-electron method, however. Consider the σ overlap of two p orbitals; as the internuclear distance R goes from 0 to ∞, the overlap integral $S_{p\sigma_A p\sigma_B}$ must change sign at some point. An approximation of type 1 constrains $H_{p\sigma_A p\sigma_B}$ to have the same nodal behavior as the overlap integral. This assumption is completely unjustified. Linderberg[2] has proposed the rotationally invariant formula

$$H_{ab} = (1/R)\,\mathrm{d}S_{ab}/\mathrm{d}R \tag{2}$$

which avoids this difficulty, but which is not in itself a satisfactory approximation for H_{ab} in an all-valence electron method.[3]

Jug[4] has established the basis for an approximate molecular orbital method based on symmetrically orthogonalized orbitals. Implementation of the method and applications to small molecules will be presented in this paper. The following sections present the derivation of a new expression for H_{ab}, its introduction into the INDO method with appropriate parameterization, and results for diatomics and triatomics.

Derivation. It is well known that interpretation of neglect of differential overlap methods on the basis of symmetrically orthogonalized orbitals provides a partial justification for such neglect. Löwdin[5] has shown that any set of linearly independent orbitals ϕ may be orthogonalized by the transformation

$$\hat{\phi} = \phi S^{-1/2}$$

$S^{-1/2}$ is defined such that $S^{-1/2}S^{-1/2} = S^{-1}$, where S^{-1} is the inverse of the overlap matrix. The set $\hat{\phi}$ has the same symmetry properties as ϕ and is as close to ϕ as possible in a least-squares fit.

In the two-orbital case, orthogonalization of orbitals $\bar{a}$ and $\bar{b}$ on atoms A and B takes the form

$$a = {}^1/_2[(1 + S_{ab})^{-1/2} + (1 - S_{ab})^{-1/2}]\bar{a} + {}^1/_2[(1 + S_{ab})^{-1/2} - (1 - S_{ab})^{-1/2}]\bar{b}$$

$$b = {}^1/_2[(1 + S_{ab})^{-1/2} + (1 - S_{ab})^{-1/2}]\bar{b} + {}^1/_2[(1 + S_{ab})^{-1/2} - (1 - S_{ab})^{-1/2}]\bar{a}$$

The core Hamiltonian integrals H_{aa} and H_{ab} over orthogonalized orbitals are related to $\bar{H}_{aa}$, $\bar{H}_{bb}$, and $\bar{H}_{ab}$ over nonorthogonal orbitals by

$$H_{aa} = (1 - S_{ab}^2)^{-1}[{}^1/_2(\bar{H}_{aa} + \bar{H}_{bb}) + {}^1/_2(1 - S_{ab}^2)^{1/2}(\bar{H}_{aa} - \bar{H}_{bb}) - S_{ab}\bar{H}_{ab}] \tag{3}$$

$$H_{ab} = (1 - S_{ab}^2)^{-1}[\bar{H}_{ab} - {}^1/_2S_{ab}(\bar{H}_{aa} + \bar{H}_{bb})]$$

Jug[3] has shown that a good approximation for $\bar{H}_{ab}$ may be derived from the commutator equation $[\mathbf{r},h] = \mathbf{p}$, where $\mathbf{r}$ is the dipole operator, h is the core Hamiltonian operator, and $\mathbf{p}$ is the linear momentum operator

$$\bar{H}_{ab} = {}^1/_2S_{ab}(\bar{H}_{aa} + \bar{H}_{bb}) + \frac{\bar{z}_{ab} - {}^1/_2S_{ab}(\bar{z}_{aa} + \bar{z}_{bb})}{(\bar{z}_{aa} - \bar{z}_{bb})}(\bar{H}_{aa} - \bar{H}_{bb}) + \frac{(1 - S_{ab}^2)}{R}\frac{\mathrm{d}S_{ab}}{\mathrm{d}R} \tag{4}$$

where the z axis is the internuclear axis and $\bar{z}_{ab} = \langle\bar{a}|z|\bar{b}\rangle$. If we expand about the center of charge (0 in Figure 1), $\bar{z}_{ab} = 0$ and $\bar{z}_{aa}$ and $\bar{z}_{bb}$ are simply the displacements of orbitals $\bar{a}$ and $\bar{b}$ from the center of charge. If we take average values of ρ_a and ρ_b for $\bar{z}_{aa}$ and $\bar{z}_{bb}$, defining ρ_a and ρ_b as absolute rather than as directed distances, we have

$$\bar{H}_{ab} = {}^1/_2S_{ab}(\bar{H}_{aa} + \bar{H}_{bb}) + \frac{\rho_b - \rho_a}{\rho_b + \rho_a}(\bar{H}_{aa} - \bar{H}_{bb}) + \frac{1 - S_{ab}^2}{R}\frac{\mathrm{d}S_{ab}}{\mathrm{d}R} \tag{5}$$

If we substitute (5) into (3) and approximate $(1 - S_{ab}^2)^{1/2} = 1 - {}^1/_2S_{ab}^2$, we get

$$H_{aa} = \bar{H}_{aa} + \frac{S_{ab}^2}{1 - S_{ab}^2}\left({}^1/_4 - {}^1/_2\frac{\rho_b - \rho_a}{\rho_a + \rho_b}\right)(\bar{H}_{aa} - \bar{H}_{bb}) - \frac{S_{ab}}{R}\frac{\mathrm{d}S_{ab}}{\mathrm{d}R} \tag{6}$$

and

$$H_{ab} = \frac{S_{ab}}{1 - S_{ab}^2}\,{}^1/_2\frac{\rho_b - \rho_a}{\rho_a + \rho_b}(\bar{H}_{aa} - \bar{H}_{bb}) + \frac{1}{R}\frac{\mathrm{d}S_{ab}}{\mathrm{d}R} \tag{7}$$

In expression 6, all terms but the first will be small unless S_{ab} is large and R is small. We therefore approximate

$$H_{aa} = \bar{H}_{aa} \tag{8}$$

which seems adequate for all molecular systems of interest with the exception of H_2, where S_{ab} is of the order of 0.75 and R of 1.4 au. Any errors introduced by the approximation in eq 8 will hopefully be accounted for in the parameterization of H_{ab}. Expressions for H_{ab} similar to (7) have been examined previously[3] and have been found to work poorly. In the derivation of (7), the term in $[S_{ab}/(1 - S_{ab}^2)]{}^1/_2(\bar{H}_{aa} + \bar{H}_{bb})$ has completely cancelled. Although (4) is a good approximation for $\bar{H}_{ab}$, (7) is not a good approximation for H_{ab}. The magnitude of H_{ab} is much smaller than that of $\bar{H}_{ab}$, and the relative error is therefore much larger. We attempt to correct this deficiency by reintroducing a part of the term that cancelled.

$$H_{ab} = \frac{{}^1/_2S_{ab}}{1 - S_{ab}^2}\left[\frac{K_a + K_b}{2}(\bar{H}_{aa} + \bar{H}_{bb}) + \frac{\rho_b - \rho_a}{\rho_a + \rho_b}(\bar{H}_{aa} - \bar{H}_{bb})\right] + \frac{1}{R}\frac{\mathrm{d}S_{ab}}{\mathrm{d}R} \tag{9}$$

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[2] J. Linderberg, *Chem. Phys. Lett.*, 1, 39 (1967).
[3] K. Jug, *Theor. Chim. Acta*, 23, 183 (1971).
[4] K. Jug, *Theor. Chim. Acta*, 30, 231 (1973).
[5] P. O. Löwdin, *J. Chem. Phys.*, 18, 365 (1950).

All that remains is to make expression 9 rotationally invariant. We allow K_i and ρ_i to depend only on the atom I to which orbital i is attached. The term $1 - S_{ab}^2$ must also be adjusted. We incorporate it into the K_I for the term in $(\bar{H}_{aa} + \bar{H}_{bb})$ and take S_{ab}^2 as the square of the s–s overlap for all orbital interactions for the term in $(\bar{H}_{aa} - \bar{H}_{bb})$. This gives as a final expression for H_{ab}

$$H_{ab} = {}^1/_2 S_{ab}\left[\frac{K_A + K_B}{2}(\bar{H}_{aa} + \bar{H}_{bb}) + \frac{1}{1 - S_{AB}^2}\frac{\rho_B - \rho_A}{\rho_A + \rho_B}(\bar{H}_{aa} - \bar{H}_{bb})\right] + \frac{1}{R}\frac{dS_{ab}}{dR} \quad (10)$$

where S_{AB} is the s–s overlap.

It is interesting to compare eq 10 with Pauling's[6] empirical formula for bond strength

$$D_{AB} = {}^1/_2(D_{AA} + D_{BB}) + k(X_A - X_B)^2 \quad (11)$$

where D_{AB} is the energy of a bond between atoms A and B, and X_A is the electronegativity of atom A. The term in $(\bar{H}_{aa} + \bar{H}_{bb})$ in (10) is, like the first term in (11), an average of the energies, and the term in $(\rho_B - \rho_A)\cdot(\bar{H}_{aa} - \bar{H}_{bb})$ in (10) in general increases as the square of the difference in electron attracting power, as does the second term in (11).

Parameterization. Expression 10 was introduced into the INDO method,[7] leaving all other features of the method untouched. The expression that (10) replaces in the original INDO method is

$$H_{ab} = {}^1/_2 S_{ab}(\beta_A{}^0 + \beta_B{}^0)$$

where $\beta_A{}^0$ and $\beta_B{}^0$ are empirical parameters. With two exceptions, values for K_I in (10) were chosen so as to duplicate the binding energies of the homonuclear diatomics. K_{Be} was taken as an intermediate between K_{Li} and K_B, and K_H was chosen to give good agreement for the binding energies of the diatomic hydrides. Values are given in Table I. From Figure 1 it seems plausible that $\bar{z}_{aa}$ and $\bar{z}_{bb}$, which ρ_A and ρ_B approximate, may on the average correspond to orbital radii. Since ρ_A and ρ_B depend only on atoms A and B, we have taken

Table I. K_I Values

I	K_I	I	K_I
H	0.100	C	0.069
Li	0.093	N	0.086
Be	0.089	O	0.072
B	0.085	F	0.054

Table II. ρ_I Values

I	ρ_I Exptl	ρ_I Adj
H_{num}	0.74	0.77
H_{den}	0.37	0.37
Li	1.34	1.34
Be	1.02	1.02
B	0.81	0.81
C	0.77	0.77
N	0.74	0.74
O	0.74	0.73
F	0.72	0.72

Table III. Diatomic Molecular Properties[a]

Mol	Equil bond length, Å			Force constant, mdyn Å			Binding energy, eV			Ionization potential, eV			Dipole moment, D					
A–B	INDO	*b*	Obsd	INDO	*b*	Obsd	INDO	*b*	Obsd	INDO	*b*	Obsd	INDO	*b*	Obsd	SCF	INDO	*b*
Li_2	2.134	2.466	2.672	0.85	0.31	0.25	14.40	1.05	1.05	13.88	3.07	4.96						
B_2	1.278	1.572	1.589	17.93	6.90	3.5	24.68	3.67	3.66	14.66	11.59							
C_2	1.148	1.231	1.242	36.3	17.3	12.2	26.55	6.46	6.36	17.23	15.80	12.0						
N_2	1.129	1.176	1.094	50.5	43.2	23.0	20.21	9.92	9.90	16.32	14.26	15.58						
O_2	1.140	1.198	1.207	54.5	45.0	11.8	15.37	5.28	5.21	14.98	15.83	12.08						
F_2	1.128	1.233	1.435	53.8	31.3	3.60	12.85	1.63	1.64	18.32	20.20	15.7						
LiH	1.572	1.739	1.595	1.94	1.51	1.03	5.71	1.78	2.52	13.02	10.32	6.5	−6.20	−6.51	−5.88	−6.00	+0.29	+0.36
BeH	1.323	1.477	1.343	5.03	2.72	2.26	7.43	1.74	2.62	9.90	9.90	8.6	−0.64	−0.98		−0.28	+0.14	+0.17
BH	1.204	1.330	1.233	8.30	6.45	3.0	9.37	3.42	3.58	11.81	11.34	9.7	−1.84	+1.17		+1.73	+0.08	+0.14
CH	1.118	1.194	1.112	11.65	9.63	4.5	8.62	3.99	3.64	13.60	13.60	10.64	+1.69	+1.58	+1.46	+1.57	−0.01	0.00
NH	1.070	1.071	1.038	14.05	16.21	5.6	6.89	5.83	3.90	17.14	15.58	13.10	+1.68	+1.97		+1.65	−0.09	−0.13
OH	1.033	1.013	0.971	16.39	18.90	7.8	6.30	6.12	4.56	18.01	16.74	13.36	+1.79	+2.06	+1.66	+2.03	−0.18	−0.22
FH	1.006	0.985	0.917	18.64	19.98	9.6	6.30	5.80	6.11	19.96	19.64	15.77	+1.98	+2.18	+1.82	+1.94	−0.27	−0.30
LiF	2.162	1.868	1.51	1.94	3.98		1.83	7.30	5.99	11.67	14.93		−7.86	−5.77	−6.6	−6.29	+0.58	+0.42
BeF	1.670	1.659	1.361	7.38	7.31	5.8	35.49	3.90	5.48	10.58	10.56		+1.96	−1.94		−1.15	−0.66	+0.35
BF	1.408	1.547	1.262	17.28	9.12	7.94	11.57	3.21	4.38	13.24	14.02		−0.86	−1.33		+0.95	+0.15	+0.36
BeO	1.474	1.429	1.331	17.30	11.25	7.5	6.11	4.17	4.69	14.19	13.85	6.0	−5.67	−4.45		−7.44	+0.39	+0.20
BO	1.300	1.424	1.331	25.26	11.08	13.6	14.75	4.17	9.22	14.22	13.74	7.0	−1.63	−0.41		−2.92	+0.19	+0.18
CO	1.196	1.272	1.128	40.46	27.16	19.0	19.82	5.48	11.22	15.56	14.79	14.01	−0.60	−0.10	+0.11	−0.27	+0.07	+0.08
NO	1.159	1.216	1.151	48.95	27.51	15.9	16.12	6.25	6.62	12.34	13.06	9.25	−0.17	−0.03		−0.32	+0.04	+0.07
BN	1.269	1.471	1.281	26.70	9.27	8.3	13.36	3.89	5.09	13.38	12.67		−0.50	+0.23			+0.03	+0.12
CN	1.174	1.231	1.172	38.88	23.77	16.3	21.58	7.15	7.63	15.56	13.78	14.2	+0.63	+0.20		−2.45	+0.05	+0.06

[a] References to all experimental values and to INDO results may be found in ref 10. The SCF dipole moments are from P. E. Cade, private communication. [b] This work.

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(6) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 92.

(7) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **47**, 2026 (1967).

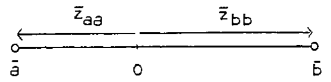
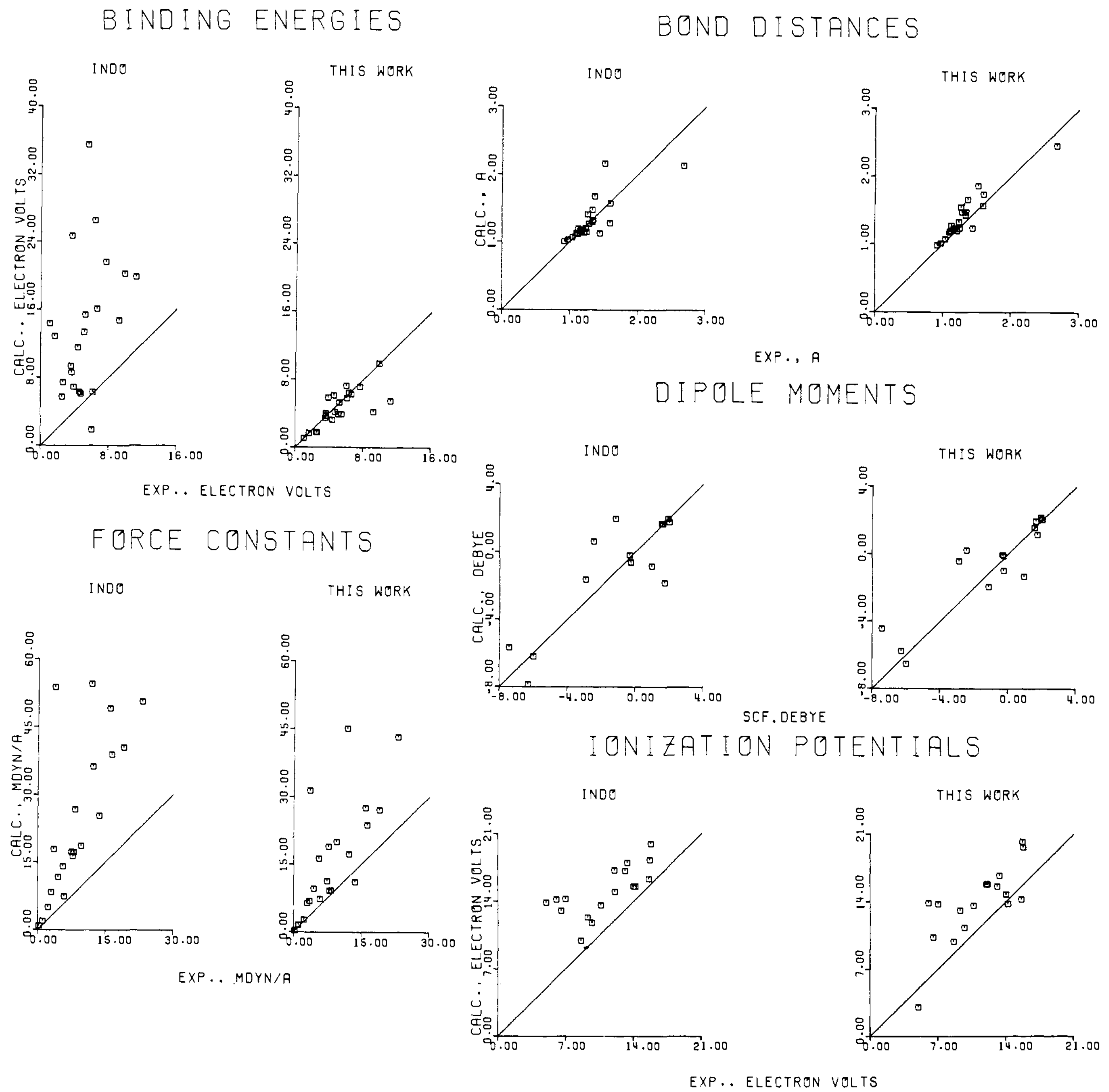


Figure 1. Diagram of the polarization factor of eq 4. 0 is the center of charge


BINDING ENERGIES

BOND DISTANCES

DIPOLE MOMENTS

FORCE CONSTANTS

IONIZATION POTENTIALS

Figure 2. Display of diatomic molecular properties as calculated by the INDO method and by this work.

them as Schomaker–Stevenson single bond radii.[8,9] These are atomic radii based on homonuclear single bonds. The value for oxygen, for example, is half the average O–O bond distance in a series of peroxides. The experimental ρ_I are given in Table II. ρ_{Be} is taken from the BeH bond distance, corrected for polarity by Pauling's empirical formula

$$R_{AB} = \rho_A + \rho_B - 0.09(X_A - X_B)^2$$

Use of single bond radii for all types of bonds should cause little problem, since the ratio $(\rho_B - \rho_A)/(\rho_A + \rho_B)$ is unchanged by a uniform scaling of ρ_A and ρ_B.

Two different values are necessary for ρ_H. The numerator in $(\rho_B - \rho_A)/(\rho_A + \rho_B)$ is a polarization term, comparing the electron-attracting power of the two atoms on the basis of their atomic radii. The expectation value of $\bar{r}$ for an electron in a Slater orbital depends on the principal quantum number n and the effective nuclear charge Z as

$$\bar{r} \sim n^2/Z$$

But the true measure of electron attraction is not Z but rather the orbital exponent ζ, where $\zeta = Z/n$. Thus

$$r \sim n/\zeta$$

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(8) V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, **63**, 37 (1941).

(9) Reference 6, p 228.

Table IV. Statistical Analysis for Diatomics[a]

Property	Av error	Rms error	% av error	% rms error
Bond distances				
INDO	0.136	0.221	10.3	16.8
This work	0.124	0.156	9.4	11.8
Force constants				
INDO	15.70	20.62	181	237
This work	8.02	11.91	92	137
Binding energies				
INDO	9.03	11.47	173	219
This work	1.68 (1.07)	2.29 (1.83)	31 (20)	44 (35)
Ioniz potentials				
INDO	3.98	4.66	36	42
This work	3.19	3.73	29	34
Dipole moments				
INDO	1.18	1.69	48	69
This work	0.97	1.41	39	57

[a] Units for the average and rms errors are the same as those in Table III. The average and rms errors have been divided by the mean of the experimental values to yield dimensionless quantities, and the result has been multiplied by 100 to give per cent average and rms errors. For dipole moments, division was by the mean of the absolute values of SCF dipoles. We have reported two sets of numbers for the analysis of binding energies calculated in this work. Twenty-two diatomics were included in the analysis. The first number in each case is based on 14 independent observations, taking into account the eight K_I values chosen to give agreement with experiment. The second number, in parentheses, is based on a full 22 independent observations. We feel this is a fairer comparison, since the effect of the eight adjustable parameters in the original INDO method is buried somewhere in the table. Since the INDO method was calibrated to give good agreement with the SCF wave function, the parameters presumably improve the dipole moments.

For the same ζ, an orbital with $n = 2$ will have twice the $\bar{r}$ value of an orbital with $n = 1$. If we identify $\bar{r}$ with ρ_I, it is essential to use twice the experimental value of ρ_H in the numerator of $(\rho_B - \rho_A)/(\rho_A + \rho_B)$. In the denominator, which is an approximation for R, the experimental value may be kept.

We make two modifications to the values of ρ_I. First, we change ρ_O from 0.74 to 0.73 to allow polarization of the N–O bond. Second, we change the numerator value of ρ_H from 0.74 to 0.77 to make the C–H bond nonpolar, in accord with the near-zero dipole moments of hydrocarbons.

Alternatively, one might parameterize expression 10 to reproduce the binding energies of minimal basis set SCF calculations. Electronic correlation could then be introduced explicitly, using either configuration interaction or one of the other correlation correction schemes.

Results

Bond lengths, force constants, binding energies, Koopmans' theorem ionization potentials, dipole moments, and atomic charges for a series of 22 diatomic molecules are listed in Table III. Figure 2 is a graphical display of these data, comparing diatomic properties predicted by the original INDO method and by this work with experimental data. In the case of dipole moments, incompleteness of experimental data and extended Hartree–Fock results has led us to compare with SCF results. As may be seen from the statistical analysis of Table IV, use of expression 10 leads to a general improvement. Binding energies and force constants are markedly better, while bond distances, ionization potentials, and dipole moments show some improvement. It is notable that the observed ground state was predicted for all diatomics using expression 10, whereas the original INDO method predicted incorrect states for B_2, BN, and NO.

Although force constants are improved, they still lack any real predictive power. We feel that most of the error here is due to the INDO approximation

$$V_{AB} = -Z_B\gamma_{AB} \qquad (12)$$

Table V. Equilibrium Bond Angles for AB_2 Molecules[a]

Molecule	State	CNDO/2	This work	Obsd	Assumed R_{AB}
CH_2	$^1A_1$	108	107	103.2	1.094
CH_2	$^3B_1$	141	141	136	1.094
NH_2	$^2B_1$	119	115	103.3	1.024
OH_2	$^1A_1$	107	111	104.5	0.960
BO_2	$^2\Pi_i$	180	180	180	1.250
CO_2^+	$^2\Pi_i$	180	180	180	1.176
CO_2	$^1\Sigma_g^+$	180	180	180	1.162
NO_2^+	$^1\Sigma_g^+$	180	180	180	1.154
CO_2^-	$^2A_1$	142	129	132	1.200
NO_2	$^2A_1$	138	129	132	1.200
NO_2^-	$^1A_1$	118	113	115.4	1.236
O_3	$^1A_1$	114	111	116.8	1.278
CF_2	$^1A_1$	105	88	100 or 108	1.320
NF_2	$^2B_1$	103	91	104.2	1.350
OF_2	$^1A_1$	99	91	103.8	1.410

[a] CNDO/2 values and references to all experimental values may be found in Pople and Beveridge, reference 10, p 91, with the exception of the experimental value for triplet CH_2; *cf.* G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971).

As R becomes small, the nuclear–electronic attraction does not increase fast enough, and the total energy consequently increases too rapidly. Approximation 12 may be responsible for the success of our approximation 8, that $H_{aa} = \bar{H}_{aa}$. The effect of orthogonalization on $\bar{H}_{aa}$ is a decrease in absolute magnitude; use of $Z_B\gamma_{AB}$ for V_{AB} has the same effect. The necessity for approximation 12 in the CNDO/2 and INDO methods may thus be interpreted as an orthogonalization effect.

A study of Table III[10] and Figure 2 shows that the errors in the properties predicted by use of expression 10 are generally systematic rather than random. Homonuclear bond distances are excellent, but heteronuclear distances are somewhat too long; predicted force constants are close to twice the experimental values; and predicted ionization potentials are about 30% too large. We believe that the systematic nature of the error indicates that our approximation for H_{ab} can correctly predict trends in molecular properties.

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(10) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, p 89.

Since many problems of chemical interest involve differences in properties rather than the properties themselves, this is of significant value.

It is also interesting that the success or failure of the different molecular properties seems to be interrelated. Take the example of BF, where the predicted bond length is too long by 0.285 Å, and the predicted dipole moment is -1.33 *vs.* the SCF moment of $+0.95$. The calculated dipole moment at the experimental bond distance is $+0.87$.

Table V gives predicted bond angles for a series of AB_2 molecules using experimental A–B bond distances. Comparison is with CNDO/2 values, as the INDO values have not been published. Agreement is satisfactory for all but the AF_2 molecules, where the predicted angles are more than 10° too small. This seems to be the result of the rapid increase of the potential attraction of one fluorine nucleus for an electron around the other fluorine nucleus upon a decrease in bond angle. These nuclear attraction terms increase the diagonal elements of the core Hamiltonian and thereby increase the off-diagonal elements as calculated by expression 10.

Recent work by Boyd and Whitehead[11] has presented a new CNDO method with much improved geometries, energies, and force constants. Their method includes 72 adjustable parameters for the first row alone, however, two for each different A–B bond. We have consequently chosen to compare our results with those of the original INDO method, since it and our method both have only eight freely adjustable parameters, one for each atom.

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[11] R. J. Boyd and M. A. Whitehead, *J. Chem. Soc., Dalton Trans.*, 73, 78, 81 (1972).

Photoelectron Spectra and MINDO–SCF–MO Calculations for Adamantane and Some of Its Derivatives[1a]

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Abstract: The high-resolution photoelectron spectra of adamantane and many of its derivatives have been determined. Eight ionization bands for adamantane are predicted by the MINDO–SCF–MO method to lie in the range 8–18 eV of the photoelectron spectrum. All of the eight bands have been identified and assigned to the appropriate molecular energy levels. The Jahn–Teller effect has been shown to be nonexistent in the degenerate ionic states of the highly symmetric adamantyl radical cation. Limited interpretations have been given for the complex photoelectron spectra of the derivatives of adamantane. In particular, the substituent effects on the ground ionic state corresponding to the highest occupied molecular orbital have been studied. The highest occupied MO of adamantane, 1-methyladamantane, 1-bromoadamantane, 2-bromoadamantane, 1-chloroadamantane, 2-fluoroadamantane, and 1-adamantane carboxylic acid is σ bonding. For methyleneadamantane the first ionization process corresponds to removal of an electron from an MO which is largely π in character. The first ionization band in the photoelectron spectra of 1-adamantanol, 2-adamantanol, adamantanone, and 2,6-adamantanedione has been assigned to a nonbonding MO primarily confined to oxygen, although in each case the "lone pair" appears to be substantially delocalized.

Adamantane is of particular interest in chemistry because of its rigid, relatively strain free diamondoid structure (Figure 1). For this reason, considerable effort has been devoted to elucidating its chemical properties.[2] The derivatives of adamantane also have been studied quite extensively,[2] and a number of interesting observations concerning adamantyl carbonium ions have been reported.[3] It generally is acknowledged that methyl groups are electron donors when attached to carbons which are sp or sp^2 hybridized, but Kwart and Miller[4] have contended that methyl groups attached to sp^3 hybridized carbons in saturated molecules can be electron withdrawing. The solvolysis work of Fort and Schleyer[3] on a series of methyl-substituted 1-adamantyl bromides supports this contention. Progressive substitution of methyl groups at the remaining bridgehead positions of 1-bromoadamantane progressively retards the solvolysis rate in ethanol.[3]

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[1] (a) A preliminary account of part of this work was presented at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, Physical Abstract 107; (b) Cleveland State University and the Chemistry Program Office, Office of Naval Research, Arlington, Virginia 22217; (c) Case Western Reserve University; (d) Kent State University.

[2] For example, see R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964), and the 149 references cited therein.

[3] For example, see R. C. Fort, Jr., and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 4194 (1964), and references cited therein.

[4] H. Kwart and J. L. Miller, *J. Amer. Chem. Soc.*, **83**, 4552 (1961).