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Original Investigations

SINDO1. A Semiempirical SCF MO Method for Molecular Binding Energy and Geometry
I. Approximations and Parametrization

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The development of a new semiempirical SCF MO method (SINDO1) at the INDO level of approximation is described. The method takes an explicit account of the orthogonality of the basis set in the calculation of core-Hamiltonian elements, approximates the effect of the explicitly ignored inner shell electrons through a pseudopotential, allows for a distinction between $p\sigma$ and $p\pi$ orbitals on an atom in the calculation of electron-nuclear attraction and employs an improved treatment of the non-diagonal core elements over the prescription used earlier in the SINDO method. A brief comparison of SINDO1 with the MINDO/3 and MNDO procedures is presented.

Key Words: A semiempirical SCF MO method ~ SINDO1.

1. Introduction

Quantitative prediction of energetic and structural features of molecules has been one of the most important objectives of quantum chemistry. Generally practical considerations force one to obtain an approximate solution using either the so called *ab initio* SCF MO technique [1–4] based on the single-determinantal approximation or the semiempirical SCF MO methods [5]. It is well known that the total molecular energies predicted even by very accurate single-determinantal *ab initio* SCF MO methods have chemically important errors because of failure to take into account electron correlation. In spite of this difficulty in predicting accurately the total energy of molecules, the energy changes associated with certain special types of chemical processes [2, 6, 7] can still be obtained with reasonable accuracy by the *ab initio* methods. The successful prediction of heats of

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reaction in these cases depends heavily on the cancellation of errors which are primarily of two different types. Firstly, by limiting the size of the basis set, *ab initio* calculations yield molecular electronic energies which are different from the exact Hartree–Fock values and this introduces inaccuracies into the calculated heats of reaction. The neglect of the effects of electron correlation is the source of further errors in the estimated heats of reaction. The choice of the basis set employed in the *ab initio* study is important for an effective cancellation of errors of the two types. Thus, a particular set may not be good in this regard for different types of reactions [2].

The semiempirical SCF MO procedures available for predicting the molecular energetic and structural features have attempted to provide theoretical frameworks which are simple and inexpensive from computational point of view and at the same time are reliable and accurate enough to be of chemical usefulness. They are based on integral approximations which simplify drastically the LCAO SCF MO treatment for molecules and employ adjustable parameters in order to enhance the accuracy of prediction. These methods are especially suitable for the study of reaction paths where investigation of the potential surface is necessary. The literature contains proposals for various semiempirical all-valence-electron SCF MO methods at different levels of approximations. The treatments developed by Fischer and Kollmar [8], Boyd and Whitehead [9] and Eaker and Hinze [10] are at the CNDO level of approximation [11], whereas MINDO/1 [12], MINDO/2 [13], MINDO/3 [14] and the SINDO [15] (symmetrically orthogonalized INDO) methods are at the INDO level [11]. Recently, Dewar and co-workers [16] have documented a more sophisticated and accurate method (MNDO) based on the NDDO approximation [11].

In this paper we present a new semiempirical SCF MO procedure (SINDO1) at the INDO level of approximation. In line with SINDO but contrary to the approach adopted in the other semiempirical treatments described above, SINDO1 takes an explicit account of the orthogonality of the basis set of atomic orbitals (AO) in the calculation of core-Hamiltonian elements involving them. In SINDO1, only the valence-shell electrons are considered explicitly in the calculation, the inner-shell electrons being treated as part of the core (frozen core approximation). The effect of the inner-shell on a "valence-electron only" calculation of the present type has been simulated through a pseudopotential term of the form suggested by Zerner [17]. This pseudopotential approximates the formation of valence basis functions which are orthogonal and non-interacting with the core. Maintaining a distinction between the $p\sigma$ and $p\pi$ orbitals on an atom in the calculation of core-Hamiltonian elements through a simple prescription is another important feature of SINDO1. Finally the CNDO/2 approximations which were still in SINDO are now modified in the spirit of CNDO/1 on the INDO level.

2. Basic Theoretical Framework

As in the original INDO prescription [11] we neglect differential overlap in all the two-electron integrals except for the one-center exchange integrals. It is well known [18] that Löwdin's symmetrically orthogonalized basis set of atomic orbitals [19] (OAO) satisfy the zero differential overlap approximation to a good degree of accuracy. While the Coulomb repulsion integrals over the OAO basis are similar in magnitude to their values in the overlapping basis [20–22], orthogonalization produces a much larger change in the core-Hamiltonian matrix elements [20, 21]. Therefore, in the present study only the core-Hamiltonian elements were interpreted over the OAO basis and the Coulomb repulsion integrals and one-center exchange integrals entering the theory were considered local in character and were estimated exactly in the same manner as in INDO [11]. Thus the Coulomb repulsion integrals between any AO of atom A and any AO of atom B were given a common value γ_{AB} and this was evaluated from the analytical formula for the two-center Coulomb repulsion integral between Slater's s-type AO's on atoms A and B. F^2 and G^1 integrals [11] used to estimate the one-center exchange integrals were those employed in INDO.

We shall next consider the diagonal and off-diagonal core-Hamiltonian matrix elements. Based on using the frozen core approximation and Zerner's form of pseudopotential to approximate the inner-shell outer-shell repulsion, core elements over the AO basis is written as

$$H_{ii} = U_i + \sum_{\mathrm{B}\neq\mathrm{A}} V_i^{\mathrm{B}} - \sum_{\mathrm{B}\neq\mathrm{A}} S_{i,1s_{\mathrm{B}}}^2 \varepsilon_{1s_{\mathrm{B}}} \quad (i \text{ on atom A}). \tag{1}$$

Here U_i represents the kinetic energy T_{ii} of an electron in AO i and its potential energy in the field of the core of the atom to which the orbital belongs. V_i^{B} is the attraction between an electron in the AO i and the core of a different atom B. The pseudopotential term (the last term in (1)) depends on the square of the overlap $S_{i,1s_{\mathrm{B}}}$ between AO i and the $1s$ AO of atom B. $\varepsilon_{1s_{\mathrm{B}}}$, which is the diagonal element of the Fock matrix for the core AO $1s_{\mathrm{B}}$, can either be chosen from X-ray data on atoms or from the molecular calculations [17].

We found it necessary to maintain a distinction between the $p\sigma$ and $p\pi$ orbitals on an atom in the calculation of core-electron attraction, V_i^{B} for an improved description of ordering of σ and π MO levels in the unsaturated molecules. By calculating $V_{p\sigma}^{\mathrm{B}}$ and $V_{p\pi}^{\mathrm{B}}$ theoretically over Slater-type AO's, this distinction was incorporated into the theory in a natural way. However, a correction to the theoretically estimated $V_{p\sigma}^{\mathrm{B}}$ and $V_{p\pi}^{\mathrm{B}}$ has been introduced in order to account for the neglect of such directional effects in the calculation of two-electron Coulomb repulsion integrals involving $p\sigma$ and $p\pi$ orbitals. We derive the form of the correction by considering a $p\sigma$ electron on atom A interacting with the core and a total number of Z_{B} valence electrons on a different atom B. The distribution of the valence electrons on atom B is averaged so that they are replaced by that of Z_{B} electrons of s-type. The repulsion between an electron in the $p\sigma$ orbital on A, denoted by $p\sigma_{\mathrm{A}}$ with this average distribution on B is $Z_{\mathrm{B}}\gamma_{p\sigma_{\mathrm{A}},s_{\mathrm{B}}}$ and the underestimate of repulsion, while using γ_{AB} (calculated as $\gamma_{s_{\mathrm{A}},s_{\mathrm{B}}}$) in place of $\gamma_{p\sigma_{\mathrm{A}},s_{\mathrm{B}}}$ is $Z_{\mathrm{B}}\,(\gamma_{p\sigma_{\mathrm{A}},s_{\mathrm{B}}} - \gamma_{\mathrm{AB}})$, which must be the correction to the theoretically calculated value for $V_{p\sigma_{\mathrm{A}}}^{\mathrm{B}}$. A similar consideration shows the correction to the theoretical value of $V_{p\pi_{\mathrm{A}}}^{\mathrm{B}}$ is $Z_{\mathrm{B}}\,(\gamma_{p\pi_{\mathrm{A}},s_{\mathrm{B}}} - \gamma_{s_{\mathrm{A}},s_{\mathrm{B}}})$. We estimate these corrections by calculating $\gamma_{s_{\mathrm{A}},s_{\mathrm{B}}}$, $\gamma_{p\pi_{\mathrm{A}},s_{\mathrm{B}}}$ and $\gamma_{p\sigma_{\mathrm{A}},s_{\mathrm{B}}}$ theoretically over Slater-type AO's.

Based on the Mulliken approximation [23] for the integrals of the form V_{ij}^{A} and the assumption [24] that the two-center kinetic energy integrals, T_{ij} are proportional to the square of the corresponding overlap integrals, S_{ij}, the expression for core elements H_{ij} can be written as

$$H_{ij} = \tfrac{1}{2}(H_{ii} + H_{jj})S_{ij} + L_{ij} \tag{2}$$

where,

$$L_{ij} = -\tfrac{1}{2}(T_{ii} + T_{jj})S_{ij}(1 - S_{ij}). \tag{3}$$

In order to account for the deficiency of the Mulliken approximation we introduce a correction to H_{ij}. The form of the correction adopted here is a modification of the expression used in the SINDO method [15]

$$\Delta H_{ij} = \tfrac{1}{4}(K_A + K_B)S_{ij}(f_A h_{ii} + f_B h_{jj}). \tag{4}$$

Here orbitals i and j belong to atoms A and B respectively. The K's are empirical parameters dependent on the nature of the atom. They have different values, K^{σ} and K^{π} for σ and π types of interactions. The condition that the expression for H_{ij} should go to that for H_{ii} when $i = j$, is satisfied only when the correction ΔH_{ij} vanishes for $i = j$. In order to fulfil this requirement we introduced the factor $f(R_{AB})$ in (4) and chose its functional form such that $f(R_{AB}) \to 0$ as $R_{AB} \to 0$. We employed a simple form

$$f(R_{AB}) = 1 - e^{-\alpha R_{AB}} \tag{5}$$

α was taken as 1 for Li and Be and 0.4 for H. For the other atoms the formula $\alpha = 4n/Z - 1$ was used. Here n is the main quantum number and Z the effective core charge. In cases where these atomic parameters did not yield good results for energies and geometries, α was adjusted empirically for particular bonds given below. Since f is different for most atoms, Eq. (4) contains implicitly a polarization term proportional to $(h_{ii} - h_{jj})$.

h_{ii} in Eq. (4) is the average of H_{ii} over all AO's of same 1 value on atom A, but neglecting the nuclear-electron attraction and pseudopotential terms which involve atoms other than A and B. Thus, for an s orbital on atom A

$$h_{s_A,s_A} = U_{s_A} + V_{s_A}^{B} - S_{s_A,1s_B}^{2}\varepsilon_{1s_B}$$

By limiting h_{ii} and h_{jj} in Eq. (4) to contain integrals involving atoms A and B only, the correction term ΔH_{ij} remains "local" in character and its improper increase in magnitude with increase in molecular size is avoided.

We shall next consider approximations to the core-Hamiltonian elements in the OAO basis $\{\lambda\}$. Starting with the Löwdin transformation [19]

$$\mathbf{H}^{\lambda} = \mathbf{S}^{-1/2}\mathbf{H}\mathbf{S}^{-1/2}$$

and a binomial expansion of $\mathbf{S}^{-1/2}$ to second order in the overlap integral, the core-Hamiltonian elements, H^{λ}_{ii} and H^{λ}_{ij} are given by [21]

$$H^{\lambda}_{ii} = H_{ii}\left(1 + \tfrac{3}{4}\sum_{j \pm i} S^2_{ij}\right) - \sum_{j \neq i} H_{ij}S_{ij} + \tfrac{1}{4}\sum_{j \neq i} S^2_{ij}H_{jj}$$
$$+ \tfrac{1}{4}\sum_{j \neq i}\sum_{k \neq i,j} [\tfrac{3}{2}H_{ij}S_{jk}S_{ki} + S_{ij}H_{jk}S_{ki} + \tfrac{3}{2}S_{ij}S_{jk}H_{ki}] \tag{6}$$

$$H^{\lambda}_{ij} = H_{ij} - \tfrac{1}{2}(H_{ii} + H_{jj})S_{ij} + \tfrac{1}{2}\sum_{k \neq i,j} [\tfrac{3}{4}S_{ik}S_{kj}(H_{ii} + H_{jj})$$
$$+ \tfrac{1}{2}S_{ik}S_{kj}H_{kk} - (H_{ik}S_{kj} + S_{ik}H_{kj})]. \tag{7}$$

The terms in the last sum in Eqs. (6) and (7) are all expected to be small. Here each product in the square bracket either involves three atomic centers or contains a core element involving two different AO's on the same atom. Neglecting these terms, expressions for H^{λ}_{ii} and H^{λ}_{ij} are simplified as

$$H^{\lambda}_{ii} = H_{ii} + \sum_{j \neq i} S^2_{ij}(\tfrac{3}{4}H_{ii} + \tfrac{1}{4}H_{jj}) - \sum_{j \neq i} H_{ij}S_{ij} \tag{8}$$

$$H^{\lambda}_{ij} = H_{ij} - \tfrac{1}{2}(H_{ii} + H_{jj})S_{ij}. \tag{9}$$

Substituting Eq. (2) into Eq. (8) we obtain

$$H^{\lambda}_{ii} = H_{ii} + \tfrac{1}{4}\sum_{j \neq i} S^2_{ij}(H_{ii} - H_{jj}) - \sum_{j \neq i} S_{ij}L_{ij}. \tag{10}$$

The terms within the second sum, involving the product of small numbers $(\frac{1}{4}S^2)$ and differences, $(H_{ii} - H_{jj})$, are likely to be small and are neglected.

Since in many cases the diagonal core elements for an s orbital, H_{ss} is higher in magnitude than that for a p orbital, H_{pp}, the second sum in Eq. (10) generally has the effect of increasing the difference between H^{λ}_{ss} and H^{λ}_{pp}, making H^{λ}_{ss} more negative. The terms in the last sum in Eq. (6), which have been neglected, have a similar effect. In order to maintain proper relative order between H^{λ}_{ss} and H^{λ}_{pp} under the neglect of such terms, we further neglect the repulsive contributing to H^{λ}_{ss} from those terms in the last sum in Eq. (10) which involve both s and p orbitals. Thus, the diagonal core elements in the OAO basis for the s orbitals are given by

$$H^{\lambda}_{s_A s_A} = H_{s_A s_A} - \sum_{B \neq A} S_{s_A s_B}L_{s_A s_B} \tag{11}$$

where the subscript s_A implies an s orbital on atom A. H^{λ}_{ii} for the p orbitals is

$$H^{\lambda}_{ii} = H_{ii} - \sum_{j \neq i} S_{ij}L_{ij}. \tag{12}$$

In order to preserve rotational invariance of the method various bicentric terms in Eq. (1) contributing to H_{ii} as well as the terms in the last sum in Eq. (12) are all calculated first in the local coordinate system and are then transformed to the molecule-fixed coordinate system. The computation time for this transformation is negligible compared to the integral calculation and SCF iteration. Substitution of H_{ij} of Eq. (2) along with the correction term of Eq. (4) into Eq. (9) leads to

$$H^{\lambda}_{ij} = L_{ij} + \tfrac{1}{4}(K_{\mathrm{A}} + K_{\mathrm{B}})S_{ij}(f_{\mathrm{A}}h_{ii} + f_{\mathrm{B}}h_{jj}). \tag{13}$$

It is of interest to compare Eq. (13) with the expression for H_{ij} which was adopted in the SINDO method [15] and was derived based on the commutator relationship $[r, h] = ip$, where r, h and p are respectively dipole, core-Hamiltonian and linear momentum operators.

Neglecting the polarization factor which involve the difference $(H_{ii} - H_{jj})$, the SINDO expression can be written as

$$H^{\lambda}_{ij} = \frac{1}{R_{\mathrm{AB}}}\frac{\mathrm{d}S_{ij}}{\mathrm{d}R_{\mathrm{AB}}} + \tfrac{1}{4}(K_{\mathrm{A}} + K_{\mathrm{B}})S_{ij}(h_{ii} + h_{jj}). \tag{14}$$

It is clear that under the restrictive conditions: $f(R_{\mathrm{AB}}) = 1$ and $K^{\sigma}_{\mathrm{A}} = K^{\pi}_{\mathrm{A}} = K_{\mathrm{A}}$, Eq. (13) goes to Eq. (14) if we substitute

$$L_{ij} = \frac{1}{R_{\mathrm{AB}}}\frac{dS_{ij}}{dR_{\mathrm{AB}}}. \tag{15}$$

Eqs. (3) and (15) provide two alternate choices for L_{ij}, but neither of them proves completely satisfactory to be useful in a semiempirical method of the present type. $(1/R)(dS/dR)$ diverges for certain interactions like those involving $1s$ and $2p\sigma$ and also $2s$ and $2p\sigma$. Thus, the behaviour of this term for these interactions at short distances is of doubtful significance. Further, unlike the case with other interactions, this term is positive for the case of two $2p\sigma$ orbitals at the distances of multiple bonds involving many of the first row atoms. In such cases there occurs a partial cancellation of terms in (13) and $H^{\lambda}_{2p\sigma_{\mathrm{A}},2p\sigma_{\mathrm{B}}}$ remains small. This leads to spurious high-lying occupied σ MO levels in several unsaturated molecules. These considerations indicate a failure of Eq. (15) for the interactions involving $2p\sigma$ orbitals. Eq. (3) is free from this limitation of Eq. (15), but proves unsatisfactory at the long distance region. A third possibility for L_{ij} would be to calculate T_{ij} of $H_{ij} = T_{ij} + V_{ij}$ exactly as linear combination of overlap integrals and V_{ij} by the Mulliken approximation. We have not pursued this alternative here, because it would introduce further integrals without assurance of a better overall balance together with Eq. (4).

As shown earlier, the form of L_{ij} as given by (3) is derived based on the assumption that the kinetic energy integral, T_{ij} is proportional to the square of the overlap, S_{ij}. This assumption is fairly accurate when two $2p\pi$ orbitals are involved, but in other cases the kinetic energy integral generally falls off faster than the square of overlap. In fact, for the $1s-1s$ case, the approximation: $T_{ij} = \frac{1}{2}(T_{ii} + T_{jj})S^{3}_{ij}$ is more appropriate. This suggests that L_{ij} should, in general, fall off with distance faster than proportional to $S(1-S)$. L_{ij} values predicted by Eq. (15) shows such a behaviour. Based on the consideration of various factors discussed above we chose L_{ij} values predicted by Eq. (15) for the $2p\pi - 2p\pi$, $2s - 2s$ and $1s - 1s$

interactions as guide in modifying Eq. (3). Unfortunately, however, we were unable to find a simple modification of Eq. (3) which is successful in reproducing the L_{ij} values obtained by Eq. (15) for all these interactions and we proceeded as follows. Noting that the one-center kinetic energy integral, T_{ii} is proportional to the square of the orbital exponent ζ_i we modified Eq. (3) as

$$L_{ij} = -\tfrac{1}{2}(\zeta_i^2 + \zeta_j^2)\frac{S_{ij}(1-S_{ij})}{1+\rho} \tag{16}$$

where, $\rho = \frac{1}{2}(\zeta_i + \zeta_j)R_{\mathrm{AB}}$.

Eq. (16) reproduces reasonably well the L_{ij} values predicted by Eq. (15) for the $2s-2s$ and $2p\pi-2p\pi$ interactions over a wide range of exponents and distances and we employed this relation for estimating L_{ij} values for the $2s-2s$, $2s-2p$, $2p\sigma-2p\sigma$ and $2p\pi-2p\pi$ and $1s-2p\sigma$ interactions. For the $1s-1s$ case we used

$$L_{ij} = -\frac{S(1-e^{-\rho})}{1+\rho} \tag{17}$$

and for the interaction $1s-2s$, average of the values of L_{ij} predicted by Eq. (16) and Eq. (17) was adopted in the present study.

We shall next discuss the choice of the quantities ζ_{A}, U_s, U_p and $\varepsilon_{1s_{\mathrm{A}}}$ for various atoms. Generally we have adopted the values suggested in the literature for these quantities, but in some cases we modified the values in order to enhance agreement with experiment in certain respects.

The orbital exponents for s and p AO's of a given atom were treated as same thus making the exponents dependent only on the nature of atom. A more sophisticated scheme could use different exponents for s and p orbitals. For Li, Be, B and C the exponents determined by minimizing the energy of isolated atoms [25] were employed, but for F, an exponent close to that obtained by Burns' rules [26] was adopted. This modification for F proved useful in providing improved results on geometry in fluorine-containing molecules. The exponents for N and O were obtained by an interpolation of the values for other atoms. For hydrogen a value close to that suggested by Fischer and Kollmar [8] has been adopted in the present study.

The one-center one-electron core integrals, U_s and U_p for various atoms, with exception of the U_s values for H, N, O and F, were estimated using the one-center exchange integrals and the average ionization potentials given by Pople and co-workers [11] and following their prescription. For U_s values of H, N, O and F somewhat higher absolute values than those obtained by the above prescription have been employed. This was achieved by adding 1.06 eV to I_{H} and 3 eV to I_s for N, O, F. The modified U_s for H led to a better description of hydrogen charges in the hydrides, whereas the changes in N and O led to improved bond angles in NH_3 and H_2O respectively.

As in the AAMOM method of Zerner [27], $\varepsilon_{1s_{\mathrm{A}}}$ values for C, N, O and F were estimated as the atomic ionization energies of $1s$ electrons obtained from ESCA.

For Li, Be, B an increase in the absolute values for ε seemed more favorable in our all valence electron method. We took $\varepsilon_{1s_{\mathrm{Li}}} = -3.5$ Hartree, $\varepsilon_{1s_{\mathrm{Be}}} = -5.02$ Hartree, $\varepsilon_{1s_{\mathrm{B}}} = -7.5$ Hartree.

In summary I_s, I_p, F^2, G^1 are taken from Pople [11] and $\varepsilon_{1s_{\mathrm{A}}}$ values are from Zerner [27], except as noted.

3. Calculation of Binding Energies and Molecular Geometries

The total energy of the molecule, E_{mol} is obtained as

$$E_{\mathrm{mol}} = \tfrac{1}{2}\sum_{i}\sum_{j} P_{ij}^{\lambda}(H_{ij}^{\lambda} + F_{ij}^{\lambda}) + \sum_{\mathrm{A}<\mathrm{B}} \frac{Z_{\mathrm{A}}Z_{\mathrm{B}}}{R_{\mathrm{AB}}^{2}}. \tag{18}$$

Here P_{ij}^{λ} and F_{ij}^{λ} are respectively the elements of the bond order and Hartree–Fock matrix. The last sum in Eq. (18) represents the potential energy of repulsion between the cores which are assumed, under the frozen core approximation, to be point charges, Z_{A}'s.

In view of the neglect of the explicit consideration of the inner-shell AO's in the calculation E_{mol} of Eq. (18) represents only the valence-electron energy. However, it has been shown [17] that the true total energy of the molecule, obtained from the calculation using a basis set expansion over the valence-shell as well as the inner-shell AO's, has the *molecular* part mainly reflected in the valence-electron energy. Thus, it is still meaningful to use E_{mol} in predicting the geometric and energetic features of molecules. The calculated binding energy, E_{B} at equilibrium geometry of a molecule is obtained as the difference between the energy of the molecule (E_{mol}) and that of its constituent atoms. The energies of atoms, E_{A} are calculated from single-determinantal wavefunctions using the same approximations and integral values as are employed in the molecular calculations.

The experimental binding energy of a molecule is obtained from its heat of formation at 0°K by subtracting the heat of formation of the constituent gaseous atoms at the same temperature (ΔHf_0^0) and the zero point vibrational energy of the molecule. E_{A} values for the various atoms are derived and ΔHf_0^0 values taken from JANAF tables [28]. A collection of values of fixed atomic parameters is presented in Table 1.

Molecular geometries were defined in terms of the internal valence coordinates (IVC), which are the bond lengths, bond angles and dihedral angles. The equilibrium geometry was determined by minimizing energy with respect to the IVC's subject to certain symmetry constraints imposed to reduce computation time. Constraints were specified based on the symmetry at the observed equilibrium geometry of the molecule. In several cases, particularly when the molecule is of low symmetry, calculations have been performed by relaxing such constraints in order to account for a possible difference between observed and predicted symmetry.

Table 1. Fixed atomic parameters (Hartree)

Atom	H	Li	Be	B
E_A	−0.52	−0.19809	−1.03379	−2.63363
Hf_0^0	0.08228	0.06061	0.12309	0.20971
U_s	−0.52	−0.19809	−0.69125	−1.39135
U_p		−0.13009	−0.54434	−1.14681
ε_{1s}		−3.5	−5.02	−7.5

Atom	C	N	O	F
E_A	−5.42015	−10.13754	−15.97148	−23.77375
Hf_0^0	0.27023	0.17927	0.09400	0.02926
U_s	−2.31446	−3.63827	−4.91604	−6.37531
U_p	−1.97826	−3.09529	−4.27909	−5.63853
ε_{1s}	−10.44	−14.66	−19.55	−25.21

The geometry optimization was carried out by an approach based on the Newton–Raphson method [29]. Denoting the IVC's by a column vector, q, the improved set of IVC's, $\mathbf{q}^{k+1}$ is generated from the old set, $\mathbf{q}^k$ by the recursion

$$\mathbf{q}^{k+1}=\mathbf{q}^k-(\mathbf{A}^k)^{-1}\mathbf{g}^k. \tag{19}$$

Here $\mathbf{g}$ is a column vector whose components are the partial derivatives of energy with respect to each of the IVC's and $\mathbf{A}$ denotes the matrix of second partial derivatives of energy

$$A_{ij}=\frac{\partial^2 E_{\text{mol}}}{\partial q_i\, \partial q_j}. \tag{20}$$

The calculation of the Hessian matrix $\mathbf{A}$ is prohibitively expensive. We, therefore, usually followed for the calculation of equilibria a simplified approach of calculating only the diagonal elements of $\mathbf{A}$ and setting its off diagonal elements to zero, thus neglecting the coupling between IVC's.

It may be mentioned that alternative procedures [8, 30], which neglect such coupling have successfully been applied to a large number of molecules. However, in certain cases, where the above approach led to difficulties in locating the minimum, optimization was carried out with the coupling elements of $\mathbf{A}$. The derivatives were calculated by finite difference from SCF calculations performed at two different displacements for each IVC. The step size of displacements were initially chosen as 0.01 Å for the lengths and 1° for the angles. For the final refinements the step size was reduced to 0.001 Å and 0.1° with the exception of some of the dihedral angles which could be optimized only with a step size of 1°. Cycling process was continued until the sum of squares of the gradients, g_i's was less than 0.00001 and $|q_i^{k+1}-q_i^k|$ was smaller than the corresponding step size for all i.

The parameters, K_A^σ and K_A^π for various atoms and α_A for different atom pairs have been adjusted, by trial and error, so as to best reproduce the binding energies

Table 2. Adjusted atomic parameters

Atom	H	Li	Be	B	C	N	O	F
ζ	1.17	0.64	0.96	1.25	1.55	1.90	2.15	2.40
K^{σ}	0.099	0.140	0.115	0.073	0.0654	0.077	0.100	0.151
K^{π}		−0.040	0.020	0	0.024	0.024	0.056	−0.025

of certain reference molecules. Reference molecules employed in the parametrization study were chosen to represent different types of bonding situations of various atoms. In view of the dependence of both the calculated binding energy and equilibrium geometry for a molecule on the parameter values, the optimization of geometry of the reference molecules and parameters were carried out simultaneously. The parameters involving C and H were first fixed from calculations on reference hydrocarbons. The parameters involving other atoms were determined, in steps, from a study on molecules containing a new atom in combination with other atoms already parametrized or from a study on molecules with a new atom pair interaction not already considered in the parametrization. Table 2 shows parameters ζ, K^{σ} and K^{π} for different atoms. Values for the bond dependence of α are given in Table 3.

4. Comparison of SINDO1 with MINDO/3 and MNDO

Of the semiempirical SCF MO methods available so far, MINDO/3 and MNDO have been most extensively applied to the study of structural and energetic features of molecules involving the first row atoms and hydrogen. Dewar and Thiel [16a] noted that MNDO represents a major improvement over MINDO/3. Its superiority was attributed [16a] to taking an improved account of the directionality of bonding by making allowance for the dependence of the bicentric two-electron integrals and core-attraction integrals on the orientation of the AO's involved. The resulting MNDO treatment is, however, much more complex than MINDO/3, for whereas MNDO requires the evaluation 22 distinct bicentric two-electron integrals for a pair of dissimilar atoms, there is only one such integral

Table 3. Adjusted bond dependent parameter α

Atom B:	H	Li	Be	B	C	N	O	F
α_H	0.8			0.5	0.362	0.425	0.5	0.55
α_{Be}			0.05					
α_B	1.0							
α_N		1.8		0.531	0.525			
α_O			0.23	0.32		0.339		
α_F		0.368	0.168	0.182	0.135	0.071	0.075	0.126

Table 4. Average errors in various semiempirical MO methods for molecules with first row atoms

		SINDO1	MINDO/3	MNDO
Length (Å)	XY	0.028(181)	0.022(91)	0.030(142)
Length (Å)	XH	0.015(105)	0.017(67)	0.017(89)
Angle (Degrees)	XYZ	2.5(53)	6.8(22)	2.8(43)
Angle (Degrees)	XYH, HXH	2.6(76)	4.1(43)	3.0(66)
Binding energy (kcal/mol)	E	8.3(132)	11.3(73)	9.0(118)
Ionization potential (ev)	I	0.80(113)	0.84(52)	0.48(67)
Dipole moment (Debye)	D	0.38(68)	0.42(34)	0.35(49)

The total number of compounds or values compared is given in parentheses

to be calculated in the INDO-based procedures like MINDO/3. SINDO1 retains the simplicity of INDO approximation in the calculation of two-electron integrals, but employs a much more elaborate prescription for estimating the core-Hamiltonian elements compared to the earlier INDO-based procedures as well as MNDO. In SINDO1 directional effects are included in various bicentric terms contributing to H_{ii} (see Eqs. (1), (11) and (12)) by making allowance for the distinction between *s*, $p\sigma$ and $p\pi$ orbitals on an atom in the treatment of such terms.

In the following papers detailed SINDO1 results for a wide range of molecules will be compared with the experimental findings and the predictions based on MINDO/3 and MNDO. Here we summarize the predictive capability of these three methods on a statistical basis. Table 4 compares the average absolute errors for various properties calculated by these methods. The available MINDO/3 data are not properly representative, making the errors quoted under MINDO/3 somewhat unreliable [32], but Dewar and coworkers [16] have concluded that MNDO represents a remarkable improvement over MINDO/3 in the accuracy of prediction of various properties. Further, MNDO is free from most of the major deficiencies or errors of MINDO/3 which are associated with the predictions on the ordering of MO levels in the unsaturated compounds, heats of formation of molecules with triple bonds and N–N bonds, heats of formation and geometry of many fluorine containing molecules and finally the bond angles. The superiority of MNDO in these areas was attributed to an inherent superiority of the NDDO approximation on which MNDO is based. It is interesting to note that the average absolute errors in binding energies [31] bond lengths and bond angles obtained from SINDO1 calculations are smaller than the average absolute errors in the corresponding quantities given by MNDO. SINDO1 and MNDO predict dipole moments with a similar accuracy, but MNDO is clearly superior for the ionization potentials calculated via Koopmans' theorem. In summarizing our findings we can state that as in MNDO, most of the major deficiencies of MINDO/3 discussed above are overcome in SINDO1. It is clear that the major achievements of MNDO have been realized in SINDO1 in a much simpler way through an improved treatment of the core-Hamiltonian elements.

References

1. H. F. Schaefer III: Critical evaluation of chemical and physical structural information, p. 591 ff, D. R. Lide, Jr., M. A. Paul, ed. Washington, D.C.: National Academy of Sciences 1974
2. Hehre, W. J., Ditchfield, R., Radom, L., Pople, J. A.: J. Am. Chem. Soc. **92**, 4796 (1970)
3. Radom, L., Lathan, W. A., Hehre, W. J., Pople, J. A.: J. Am. Chem. Soc. **93**, 5339 (1971)
4. Hariharan, P. C., Pople, J. A.: Chem. Phys. Letters **16**, 217 (1972)
5. Jug, K.: Theoret. Chim. Acta (Berl.) **14**, 91 (1969)
6. Snyder, L. C.: J. Chem. Phys. **46**, 3602 (1967)
7. Snyder, L. C., Basch, H.: J. Am. Chem. Soc. **91**, 2189 (1969)
8. Fischer, H., Kollmar, H.: Theoret. Chim. Acta (Berl.) **13**, 213 (1969)
9. Boyd, R. J., Whitehead, M. W.: J. Chem. Soc., Dalton Trans. 73, 78, 81 (1972)
10. Eaker, C. W., Hinze, J.: J. Am. Chem. Soc. **96**, 4084 (1974)
11. Pople, J. A., Beveridge, D. L.: "Approximate molecular orbital theory", New York: McGraw-Hill 1970
12. Baird, N. C., Dewar, M. J. S.: J. Chem. Phys. **50**, 1262 (1969)
13. Dewar, M. J. S., Haselbach, E.: J. Am. Chem. Soc. **92**, 590 (1970)
14. Bingham, R. C., Dewar, M. J. S., Lo, D. H.: J. Am. Chem. Soc. **97**, 1285, 1294, 1302, 1307 (1975); Dewar, M. J. S., Lo, D. H., Ramsden, C. A.: J. Am. Chem. Soc. **97**, 1311 (1975)
15. Coffey, P., Jug, K.: J. Am. Chem. Soc. **95**, 7575 (1973)
16. a. Dewar, M. J. S., Thiel, W.: J. Am. Chem. Soc. **99**, 4899, 4907 (1977); b. Dewar, M. J. S., McKee, M.: J. Am. Chem. Soc. **99**, 5231 (1977); c. Dewar, M. J. S., Rzepa, H. S.: J. Am. Chem. Soc. **100**, 58, 777 (1978)
17. Zerner, M. C.: Mol. Phys. **23**, 963 (1972)
18. Löwdin, P. O.: Proc. Int. Conf. Theoret. Phys. Kyoto, Tokyo, 1953, 599 (1954); McWeeny, R.: Proc. Roy. Soc. (London) **A227**, 288 (1955); Fischer-Hjalmars, I.: J. Chem. Phys. **42**, 1962 (1965)
19. Löwdin, P. O.: J. Chem. Phys. **18**, 365 (1950)
20. Chong, D. P.: Mol. Phys. **6**, 67 (1965)
21. Brown, R. D., Roby, K. R.: Theoret. Chim. Acta (Berl.) **16**, 175 (1970)
22. Roby, K. R.: Chem. Phys. Letters **11**, 6 (1971)
23. Mulliken, R. S.: J. Chim. Phys. **46**, 497 (1949)
24. Ruedenberg, K.: J. Chem. Phys. **34**, 1892 (1961); Cusachs, L. C., Cusachs, B. B.: J. Phys. Chem. **71**, 1060 (1967)
25. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
26. Burns, G.: J. Chem. Phys. **41**, 1521 (1964)
27. Zerner, M.: J. Chem. Phys. **62**, 2788 (1975)
28. Stull, D. R., Prophet, H.: JANAF Thermochemical tables. Washington, D.C.: NBS. 1971
29. Himmelblau, D. M.: Applied nonlinear programming. New York: McGraw-Hill 1972
30. Newton, M. D., Lathan, W. A., Hehre, W. J., Pople, J. A.: J. Chem. Phys. **52**, 4064 (1970)
31. The error in SINDO1 molecular binding energies has been compared here with the error in the heats of formation given by MINDO/3 and MNDO
32. The superior XY bond lengths of MINDO/3 seem fortuitous, considering that few fluorine, no boron or beryllium compounds could be included. Without compounds containing F, B, Be SINDO1 has the same average error as MINDO/3.

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