A Semi-empirical NDDO Method for All-valence-electron Systems. I. Hydrocarbons

Osamu KIKUCHI

Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 300-31

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A semi-empirical NDDO method is applied to the evaluation of the molecular geometries and excitation energies of a variety of hydrocarbons, both saturated and conjugated, and of the heats of reactions among these hydrocarbons. Two-center electron repulsion integrals are evaluated by the simple formulae derived from the corresponding theoretical formulae. The off-diagonal core matrix elements and core-core repulsion energies are estimated empirically. It is shown that the method gives good estimates of the molecular geometries and excitation energies and permissible values for the heats of reactions.

The understanding of a chemical reaction process requires a knowledge of the potential energy surfaces for the lowest and excited states. The MO method to be used in the study of a reaction process should well reproduce three quantities at the same time; the molecular geometries, the heats of reaction, and the excitation energies of the molecules. Many semi-empirical methods for all-valence-electron systems have been reported,[1-5] and the recent MINDO/3 version, in which a large number of parameters are introduced, reproduces satisfactorily the ground-state properties of molecules.[3] However, little attention has been paid to the simultaneous evaluation of the above three quantities. This paper will search for a semi-empirical method, which is at the same level of parametrization as in the MINDO/2 method,[4] and which gives good estimates of the above three quantities.

Most of the semi-empirical methods for all-valence electrons are modified versions of the CNDO and INDO approximations, while only a few are those of the NDDO (Neglect of Diatomic Differential Overlap) approximation.[5] The NDDO approximation may be difficult to parametrize or for use in evaluating a large number of additional integrals semi-empirically. However, it represents a more logical solution of the problem[6] than the CNDO and INDO approximations. In this study, the NDDO approximation was used. Two-center integrals were evaluated by the simple formulae which were derived from the corresponding theoretical formulae. Parameters were chosen so as to give, at the same time, well-balanced values for the above three quantities. The method was applied to several hydrocarbons, and the results were compared with the observed values.

Method

The LCAO-MO's for valence electrons are determined from Roothaan's LCAO-SCF equation.[7] The atomic integrals necessary for the calculation are evaluated by the following methods.

One-center electron repulsion integrals are evaluated from the Slater-Condon parameters, F_K and G_K, as in MINDO/2.[4]

Two-center electron repulsion integrals are evaluated from the integrals related to the local diatomic coordinate. Consider the integrals between AO's of two atoms, A and B:

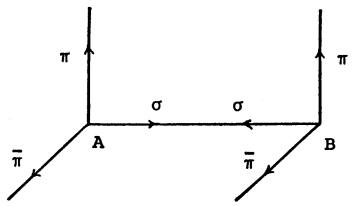

Fig. 1. Local diatomic coordinate and AO's of atoms A and B.

$$(\mu^A\nu^A|\lambda^B\sigma^B) \equiv \int \phi_\mu{}^A(1)\phi_\nu{}^A(1)\frac{1}{r_{12}}\phi_\lambda{}^B(2)\phi_\sigma{}^B(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \quad (1)$$

First, we transform the AO's, ϕ_μ's, into the local coordinate system of Fig. 1. The repulsion integrals of the original AO's can be expressed in terms of integrals between the transformed AO's. The integrals between the AO's of Fig. 1 are given by Roothaan.[8] In Roothaan's formulae, if the terms higher than the third order in $1/R_{AB}$ (R_{AB} is the distance between two atoms, A and B) are neglected, the integrals between the AO's of Fig. 1 are written as:

$$\begin{aligned}
&(s^As^A|s^Bs^B) \equiv \gamma_{AB}\\
&(\sigma^A\sigma^A|\sigma^B\sigma^B) = \gamma_{AB} + 6I_1\\
&(s^As^A|\sigma^B\sigma^B) = \gamma_{AB} + 3I_1\\
&(\sigma^A\sigma^A|\pi^B\pi^B) = \gamma_{AB} + \frac{3}{2}I_1\\
&(s^As^A|\pi^B\pi^B) = \gamma_{AB} - \frac{3}{2}I_1\\
&(\pi^A\pi^A|\pi^B\pi^B) = (\pi^A\pi^A|\bar{\pi}^B\bar{\pi}^B) = \gamma_{AB} - 3I_1\\
&(s^A\sigma^A|s^Bs^B) = (s^A\sigma^A|\sigma^B\sigma^B) = (s^A\sigma^A|\pi^B\pi^B) = I_2\\
&(s^A\pi^A|s^B\pi^B) = I_3\\
&(s^A\sigma^A|s^B\sigma^B) = I_4\\
&(\sigma^A\pi^A|\sigma^B\pi^B) = (\pi^A\bar{\pi}^A|\pi^B\bar{\pi}^B) = (s^A\pi^A|\sigma^B\pi^B) = 0
\end{aligned} \quad (2)$$

where s^A is the 1s or 2s AO of the A atom and where σ^A and π^A are the $2p\sigma$ and $2p\pi$ AO's of the A atom. They are defined in the local coordinate (Fig. 1). The I_i's are sub-integrals defined by Roothaan:

$$\begin{aligned}
I_1 &= [3S|3D\Sigma]\\
I_2 &= \frac{5}{2\sqrt{3}}[3S|3P\Sigma]\\
I_3 &= \frac{25}{12}[3P\Pi|3P\Pi]\\
I_4 &= \frac{25}{12}[3P\Sigma|3P\Sigma]
\end{aligned} \quad (3)$$

The sub-integral $[3S_a|3D\Sigma_b]$ is different from $[3S_b|3D\Sigma_a]$ when the A and B atoms are of different species. In the above formulae, this difference is neglected, though, and both are written as I_1.

The integrals between s orbitals, γ_{AB}, are calculated by using the Ohno-Klopman expression.[9] The sub-integrals, I_i's, are calculated by means of the following formulae:

$$\begin{aligned} I_1 &= 19.294 f R_{AB}\gamma_{AB}^4 \\ I_2 &= 1481.9 f R_{AB}\gamma_{AB}^3 \\ I_3 &= 0.5 I_4 = 52.263 f R_{AB}\gamma_{AB}^4 \end{aligned} \tag{4}$$

where $f=(F_2^A+F_2^B)/(F_0^A+F_0^B)$[5]. An explanation of these formulae is given in the Appendix. The values of the repulsion integrals calculated from (2) were compared with the theoretical values (Table 1). All two-center repulsion integrals (1) between the original AO's can be evaluated from the above integrals by means of:

$$\begin{aligned} &(s^A s^A|s^B s^B) = \gamma_{AB} \\ &(s^A s^A|s^B p_k^B) = a_{k\sigma} I_2 \\ &(s^A s^A|p_k^B p_l^B) = \delta_{kl}\gamma_{AB} + \frac{3}{2} I_1\{3a_{k\sigma}a_{l\sigma} - \delta_{kl}\} \\ &(s^A p_i^A|s^B p_k^B) = I_3\{\delta_{ik} + 3a_{i\sigma}a_{k\sigma}\} \\ &(s^A p_i^A|p_k^B p_l^B) = \delta_{kl}a_{i\sigma}I_2 \\ &(p_i^A p_j^A|p_k^B p_l^B) = \delta_{ij}\delta_{kl}\gamma_{AB} + \frac{I_1}{2}\{-6\delta_{ij}\delta_{kl} \\ &\qquad + 9\delta_{ij}a_{k\sigma}a_{l\sigma} + 9\delta_{kl}a_{i\sigma}a_{j\sigma}\} \end{aligned} \tag{5}$$

where s represents the s AO, and p_i, one of the $2p_x$, $2p_y$, and $2p_z$ AO's defined in the original coordinate. The $a_{i\sigma}$ is scalar product of two vectors, $\mathbf{e}_i$ and $\mathbf{e}_{AB}$, the unit vector directed along the i-axis and that directed from A toward B respectively. These expressions satisfy the correct transformation condition which ensures the invariance with respect to the rotation of axes.

TABLE 1. VALUES OF CARBON-CARBON TWO-CENTER REPULSION INTEGRALS FOR $R_{CC}=1.50$ Å.

Type	Values of integrals	
	Calcd using Slater AO's	Calcd from (2)—(4)
$(ss\|ss)$	9.21 eV	7.26 eV
$(\sigma\sigma\|\sigma\sigma)$	10.94	8.11
$(ss\|\sigma\sigma)$	9.99	7.68
$(\sigma\sigma\|\pi\pi)$	9.51	7.47
$(ss\|\pi\pi)$	8.82	7.05
$(\pi\pi\|\pi\pi)$	8.56	6.83
$(\pi\pi\|\bar{\pi}\bar{\pi})$	8.38	6.83
$(s\sigma\|ss)$	2.41	1.50
$(s\sigma\|\sigma\sigma)$	2.77	1.50
$(s\sigma\|\pi\pi)$	2.23	1.50
$(s\sigma\|s\sigma)$	0.96	0.76
$(s\pi\|s\pi)$	0.78	0.38

The attraction $(\phi_\mu^A|V_B|\phi_\mu^A)$ between an electron in an AO ϕ_μ on the A atom and the core of the B atom was assumed to be:

$$(\phi_\mu^A|V_B|\phi_\mu^A) = -Z_B(\phi_\mu^A\phi_\mu^A|s^B s^B) \tag{6}$$

where $Z_B e$ is the core charge of the B atom. In the NDDO approximation, the attraction $(\phi_\mu^A|V_B|\phi_\nu^A)$ is also taken into account. This was assumed to be:

$$(\phi_\mu^A|V_B|\phi_\nu^A) = -Z_B(\phi_\mu^A\phi_\nu^A|s^B s^B) \tag{7}$$

by analogy with the diagonal parts. From these approximations, the core matrix elements between AO's on the same atom is written as:

$$H_{\mu\nu} = \delta_{\mu\nu}U_{\mu\mu} - \sum_{B(\neq A)} Z_B(\phi_\mu^A\phi_\nu^A|s^B s^B) \tag{8}$$

where $U_{\mu\mu}$ is the diagonal matrix element of ϕ_μ with respect to the one-electron Hamiltonian containing only the core of its own atom, the values of which are given by Baird and Dewar.[4] The off-diagonal elements between AO's on the different atoms are calculated by means of:

$$H_{\mu\nu} = \frac{1}{2}S_{\mu\nu}(\beta_\mu+\beta_\nu) \tag{9}$$

where $S_{\mu\nu}$ is the overlap integral and β_μ is a parameter which is empirically determined.

The core repulsion energy between the A and B atoms, *i.e.*, E_{core}^{AB}, must be equal to the electron-electron repulsion energy between the neutral atoms when $R_{AB}\to\infty$. $R_{AB}\to 0$, E_{core}^{AB} should tend to infinity. Many parametric expressions for E_{core}^{AB} which satisfy these conditions are possible. The following simple expressions are used in the present study:

$$\begin{aligned} E_{ore}^{AB} &= Z_A Z_B \gamma_{AB} && (R_{AB}>R_0) \\ E_{core}^{AB} &= Z_A Z_B\left\{\frac{b}{R_{AB}^a}+c\right\} && (R_{AB}<R_0) \end{aligned} \tag{10}$$

The constant, c, is determined by fitting values calculated from the two equations at $R_{AB}=R_0$. The a, b, and R_0 parameters are determined empirically.

Results and Discussion

The excitation energies of six hydrocarbons (CH_4, C_2H_6, C_3H_8, C_2H_4, C_4H_6, and C_2H_2) were calculated by the CI method, in which only singly excited configurations were taken into account in the evaluation of the singlet excited states. The relation between the values of β_μ and the excitation energies of these compounds was examined. The values of $\beta_{1s}(H)=-7.3$ eV, $\beta_{2s}(C)=-13.8$ eV, and $\beta_{2p}(C)=-9.5$ eV gave the best fit of the calculated excitation energies with the observed values. These β_μ values, however, were not appropriate for the estimation of the molecular geometries and heats of reactions. A compromise was thus made for the values of β_μ, and the values listed in Table 2 were used in all the calculations in this paper.

TABLE 2. VALUES OF β_μ(eV)

	1s(H)	2s(C)	2p(C)
β_μ	−7.5	−13.2	−9.3

In order to determine the parameters in the core-core repulsion energy (10), the calculated geometries of the above six hydrocarbons and the heats of reactions among them were compared with the observed values. The parameters were determined with the help of the

Table 3. Parameters in core-core repulsion formulae (10)[a]

	a	b	R_0
H-H	10.45	0.7436	2.642
H-C	14.00	0.5034	2.779
C-C	13.16	0.4899	3.621

a) The core-core repulsion energies calculated from the parameters are in eV units.

Davidon-Fletcher-Powell minimization technique.[10,11] They are listed in Table 3.

Molecular Geometry. The molecular geometries of typical hydrocarbons were calculated using the parameters determined above. They are listed in Table 4. The C–C and C=C bond lengths calculated agreed with the observed values within 0.03 Å (mean deviation; 0.01 Å), while the C≡C bond lengths were smaller than the observed values by 0.05 Å. The C–H bond lengths estimated agreed with the observed values within 0.01 Å. The bond angles also agreed well with the observed values (within 1 degree) except for the HCH angles; they were slightly smaller than the observed values. It seems that the present NDDO method predicts the geometries of hydrocarbons correctly.

Table 4. Calculated equilibrium geometries of hydrocarbons[a]

Compound	Type	Expt[12]	Calcd
Methane	C–H	1.091	1.090
Ethane	C–C	1.536	1.517
	C–H	1.107	1.095
	HCC	110.5	110.0
Propane	C–C	1.526	1.528
	C–H	1.091	1.098
	HCC	111.8	111.1
	CCC	112.4	111.4
Ethylene	C=C	1.332	1.315
	C–H	1.084	1.091
	HCH	115.4	112.5
Propene[b]	C–C	1.488	1.517
	C=C	1.353	1.324
	CCC	124.8	123.1
s-trans-Butadiene	C–C	1.483	1.483
	C=C	1.337	1.331
	CCC	122.4	123.9
Acetylene	C≡C	1.205	1.158
	C–H	1.059	1.069
Propyne[b]	C–C	1.459	1.466
	C≡C	1.206	1.162
Allene	C=C	1.308	1.292
	C–H	1.081	1.093
	HCH	116.0	110.8
Cyclopropane	C–C	1.524	1.531
	C–H	1.092	1.104
	HCH	118.2	106.1
Cyclobutane[b]	C–C	1.548	1.548
Cyclopropene[b]	C–C	1.525	1.514
	C=C	1.286	1.311
Cyclobutene[b]	C–C	1.551[c]	1.560
	=C–C	1.523[c]	1.530
	C=C	1.325[c]	1.343

a) Bond lengths in Å; bond angles in degrees. b) Geometries of CH(sp) and CH_2(sp^2, sp^3) groups were assumed to be those of acetylene, ethylene and cyclopropane. c) Estimated from Ref. 13.

Heats of Reactions. The heats of reactions among the above hydrocarbons were estimated by using the geometries obtained in the previous section (Table 5). The energy difference between *s-trans-* and *s-cis-*butadiene was correctly estimated. The agreement of the heats of the hydrogenations of unsaturated hydrocarbons with the observed values was not satisfactory, however, (the mean deviation for 8 examples was 7 kcal/mol). Considerable disagreements were found in the hydrogenations and additions related to ethylene or cyclic compounds. This comes form the fact that the calculated energy of ethylene is high (≈15 kcal/mol unstable) in comparison with other compounds, while those of cyclic compounds are quite low (stable).

Table 5. Calculated heats of reactions[a]

Reactions	Expt[14]	Calcd[b]
Hydrogenations		
acetylene → ethane	74.4	73.6
ethylene → ethane	32.7	47.6
propyne → propane	69.1	54.9
propene → propane	29.7	38.0
cyclopropene → cyclopropane	43.9	46.2
cyclobutene → cyclobutane	31.1	38.2
cyclopropane → propane	37.5	29.9
allene → propene	41.0	33.9
Isomerizations		
s-trans-butadiene → *s-cis*-butadiene	2.2	2.9
allene → propyne	1.6	17.0
cyclopropane → propene	7.8	−8.1
Additions		
acetylene + ethylene → *s-trans*-butadiene	40.4	51.8
acetylene + methane → propene	31.4	34.6
ethylene + methane → propane	30.2	46.6

a) Heats of reactions in kcal/mol. b) The molecular geometries listed in Table 4 were used in the calculation.

Excitation Energy. The excitation energies of several hydrocarbons were calculated by the CI method using their calculated geometries. In the CI calculation, only singly excited configurations were taken into account. The excitation energies are listed in Table 6. The MINDO/2 method, which includes parameters comparable to the present NDDO method and gives good estimates for the molecular ground-state properties, gives poor excitation energies. This is an obstacle to its application to photochemical reactions. The excitation energies obtained by the NDDO method agree with the observed values within 0.5 eV, however; this deviation is permissible in studies of photochemical processes.

Since a properly parametrized version of NDDO should be superior to a similar parametric version of

TABLE 6. LOWER THREE EXCITED SINGLET STATES AND THE LOWEST TRIPLET STATE OF HYDROCARBONS (eV)

Compound	Excited states	Calcd	Obsd[15]	MINDO/2
Methane	$^1T_2$	9.49	9.71	7.41
	$^1T_2$	11.02		
	$^1T_1$	11.27		
	$^3T_2$	8.15		
Ethane	^1E_u	9.01	9.40	6.24
	^1E_g	9.46		
	$^1A_{2u}$	9.70		
	^3E_u	8.42		
Propane	$^1B_1$	8.79	8.89	6.06
	$^1A_1$	9.23		
	$^1B_2$	9.27		
	$^3B_1$	8.03		
Ethylene	$^1A_{2g}(\sigma\rightarrow\pi^*)$	6.37		
	$^1B_{1g}(\pi\rightarrow\sigma^*)$	7.21		
	$^1B_{1u}(\pi\rightarrow\pi^*)$	7.45	7.6	5.32
	$^3B_{1u}(\pi\rightarrow\pi^*)$	3.09		
trans-Butadiene	$^1B_u(\pi\rightarrow\pi^*)$	5.91	6.0	4.93
	$^1A_u(\sigma\rightarrow\pi^*)$	6.03		
	$^1A_u(\pi\rightarrow\sigma^*)$	6.73		
	$^3B_u(\pi\rightarrow\pi^*)$	2.21		
Acethelene	$^1\Sigma_u$	5.73	5.23	4.13
	$^1\Delta_u$	6.29		
	$^1\Pi_u$	7.51		
	$^3\Sigma_u$	4.56		

INDO, it seems that the present NDDO method is not completed in its parametrization. However, it gives good estimates of the molecular geometries and excitation energies of hydrocarbons and permissible values of the heats of reactions among them. It may be fit for the evaluation of potential energy surfaces related to both thermal and photochemical reactions.

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Appendix

An explanation of Eqs. 4 will be given here. Consider the sub-integral $[3S|3D\Sigma]$ between carbon atoms. When $\rho \gg 1$ ($\rho \equiv R_{AB}(\zeta_A+\zeta_B)/a_0$, and when $R_{CC}=1.0$ Å corresponds to $\rho \simeq 6$), this is approximately expressed by:

$$[3S|3D\Sigma] \simeq \zeta/\rho^3 \qquad \text{(A-1)}$$

This means that the integral is approximated by a function of $\gamma_{CC}{}^3$ from the present semi-empirical point of view:

$$I_1 = c_1 R \gamma_{CC}^4 \qquad \text{(A-2)}$$

where $R\gamma_{CC}$ was introduced so that $I_1 \rightarrow 0$ when $R_{CC}\rightarrow 0$. To determine the coefficient, c_1, the sub-integral, $[3D\Delta|3D\Delta] \lesssim \zeta/\rho^5$, was approximated as a function of $\gamma_{CC}{}^5$:

$$[3D\Delta|3D\Delta] = c_2 \gamma_{CC}^5 \qquad \text{(A-3)}$$

If the present semi-empirical values of $[3D\Delta|3D\Delta]$ (namely$=4/27(pp'|pp') \propto F_2{}^C$) and γ_{CC} ($=F_0{}^C$) at $R_{CC}=0$ are used in (A-3), the relation between c_2 and the Slater-Condon parameters is obtained:

$$c_2 \propto (F_2{}^A+F_2{}^B)/(F_0{}^A+F_0{}^B)^5 \qquad \text{(A-4)}$$

where A and B represent two carbon atoms. The theoreoretical formulae indicate that the $[3S|3D\Sigma] \simeq [3D\Delta|3D\Delta]|\rho^2$ relation holds approximately.[8] Thus, the I_1 integral was expressed as:

$$I_1 = c_3 \frac{F_2{}^A+F_2{}^B}{(F_0{}^A+F_0{}^B)^5} R_{AB}\gamma_{AB}^4 \qquad \text{(A-5)}$$

The c_3 coefficient was determined by means of the following equation, the integral being evaluated at $R_{CC}=1.50$ Å:

$$(I_1{}^{theor}/I_1{}^{emp}) = (\gamma_{AB}{}^{theor}/\gamma_{AB}{}^{emp})^3 \qquad \text{(A-6)}$$

Though (A-5) is obtained from the carbon-carbon pair, (A-5) will be used for the integrals between other atomic pairs. The "$F_2{}^H$" value was estimated using the I_2 formula of (4) and an equation similar to (A-6); $F_2{}^H=7.802$ eV was obtained.

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