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Semi-Empirical SCF MO Method for Systems Including All Valence Electrons

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For the purpose of evaluating approximate SCF-MO's for systems including all valence electrons, two semi-empirical methods are presented. One of them (method I) uses non-empirical Coulomb integrals and the other (method II) empirical ones. The orbital energies, charge distributions, and excitation energies are calculated for ethylene, acetylene formaldehyde, carbon monoxide and hydrogen cyanide, and are compared with those obtained by the other semi-empirical and non-empirical calculations and also with the corresponding experimental values. The present methods are found to give rather satisfactory results. The calculated orbital energies are improved by the present methods compared with those by the CNDO type calculation. Calculated charge distributions are well coincident with those of the non-empirical SCF calculation. Calculated dipole moments change in parallel with experimental values from a molecule to another, though the former values are generally larger than the latter.

It is desirable to develop a theoretical method convenient for the quantitative or semi-quantitative treatment of all valence electrons of complex molecules. Yoshizumi[1] and also Hoffman[2] extended the simple Hückel method to σ-electron systems

1) H. Yoshizumi, *Trans. Faraday Soc.*, **53**, 125 (1957).

2) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963).

in spite of several difficulties[3] inherent to the method. More quantitative theories for all valence electrons analogous to the Pariser-Parr-Pople[4] method for π-electrons were developed.[5-13]

One of them is the CNDO (Complete Neglect of Differential Overlap) method developed by Pople, Santry and Segal.[8,9] This method, in spite of its simplicity, brought about much success in explaining several points such as the charge distributions of diatomic molecules and the bending force constants of AH_2 and AH_3 type molecules (A; C, N and O). It failed, however, in explaining several problems, for example, the streching force constants[9] or the charge densities at hydrogen atoms for a series of CH_4, C_2H_6, C_2H_4 and C_2H_2.[10]

Several other methods[14-16] are presented along the lines of considering all valence electrons and of evaluating semiempirically Coulomb integrals. Yonezawa *et al.*[16] obtained rather satisfactory results for charge distributions, ionization potentials and excitation energies by the aid of the method (called hereafter the Y-Y-K method) developed on this line. But in details there are still several difficulties; for example, the orbital energy separation is usually too small compared with those obtained by the exact non-empirical SCF calculation. This seems to be mainly due to the use of empirical Coulomb integrals. In this connection, the following points may be pointed out as the problem of the CNDO and Y-Y-K method. It may be expected[17] that σ-orbitals are more closely packed than π-orbitals and therefore that the Coulomb integrals are larger for σ-electrons than for π-electrons. In the CNDO method all one-center Coulomb integrals are taken to be equal to one another and two-center Coulomb integrals are independent of the character of atomic orbitals. In the Y-Y-K method, one-center Coulomb integrals are evaluated differently for s and p orbitals but the individuality of two-center Coulomb integrals is not considered except for the cases where one-center integrals are different. This effect is expected to be especially great for the molecules which have both σ- and π-electrons.

In this paper, we present improved semi-empirical methods suitable to the theoretical treatment of systems including all valence electrons and compare the results obtained for some small molecules with those by the other methods.

Theoretical

Roothaan's equation of LCAO SCF[18] is employed, the atomic integrals necessary for the calculation being evaluated by the following two methods. In method I, the integrals are evaluated approximately but non-empirically except for off-diagonal core integrals; in method II, the integrals are evaluated empirically. The essential points of our calculation are described below.

1. Molecular orbitals are expressed as linear combinations of all the valence atomic orbitals (AO's) centered on each atom except for the 1s orbitals of carbon, nitrogen and oxygen which are pushed into the cores. The Slater type AO's are taken, if necessary, the orbital exponent being determined by Slater's rule except for the hydrogen 1s AO, the effective nuclear charge of which is taken to be 1.2.

2. In Roothaan's equation,[18] the overlap integrals and two-electron integrals including two-center differential overlap are disregarded. This means that all the one-center integrals and the Coulomb type two-center integrals are taken into account in the present calculation.

3. The one-center core integrals are calculated non-empirically in method I with the core Hamiltonian H^{core};

$$H^{\text{core}} = \sum_{\mu} H_{\mu}^{\text{core}} = \sum_{\mu}\left[-\frac{1}{2}A_{\mu} - \sum_{A}\frac{Z_A}{R_{A\mu}}\right] \qquad (1)$$

where Z_A is taken as the number of valence electrons in atom A and $R_{A\mu}$ is the distance between the μth electron and atom A. But for 2s orbital, a different method based on the experimental ionization potentials (I.P.) are used as follows;

$$\langle 2s|H^{\text{core}}|2s\rangle = \langle 2p|H^{\text{core}}|2p\rangle + (\text{I.P.}(2s) - \text{I.P.}(2p)) \qquad (2)$$

In method II, this integral for AO x is evaluated

3) K. Morokuma, H. Kato, T. Yonezawa and K. Fukui, This Bulletin, **38**, 1263 (1965).

4) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 416 (1953), J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

5) H. A. Pohl, R. Rein and K. Appel, *J. Chem. Phys.*, **41**, 3385 (1964).

6) N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, **87**, 1227 (1965).

7) S. Katagiri and C. Sandorfy, *Theor. Chim. Acta*, **4**, 203 (1966).

8) J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **43**, s129 (1965).

9) J. A. Pople and G. A. Segal, *ibid.*, **43**, s136 (1965); *ibid.*, **44**, 3289 (1966).

10) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

11) D. W. Davis, *Chem. Phys. Lett.*, **2**, 173 (1968).

12) J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, **11**, 239 (1968).

13) J. M. Sichel and M. A. Whitehead, *ibid.*, **11**, 254 (1968).

14) G. Klopman, *J. Amer. Chem. Soc.*, **86**, 4550 (1964).

15) M. J. S. Dewar and G. Klopman, *ibid.*, **89**, 3089 (1967); **89**, 3966 (1967).

16) T. Yonezawa, K. Yamaguchi and H. Kato, This Bulletin, **40**, 536 (1967).

17) See, for example, B. J. Ransil, *Rev. Mod. Phys.*, **32**, 245 (1960).

18) C. C. J. Roothaan, *ibid.*, **23**, 69 (1951).

$$\langle x|H^{\mathrm{core}}|x\rangle = -\mathrm{I.P.}(x) - \sum_{i\neq x} n_i\left\{(xx|ii) - \frac{1}{2}(ix|ix)\right\} \quad (3)$$

where n_i is the occupation number of the ith orbital and the summation is taken over all valence orbitals.

4. One-center Coulomb integrals are estimated non-empirically in method I by using the Slater type functions.

In method II, the Pariser approximation[19] is used for (pp|pp) type integral. Since the valence states of atoms, particularly of hetero-atoms can not be determined exactly, we assume the following valence states:*1 sp^3 for carbon, sp^4 for nitrogen and s^2p^4 for oxygen. The other one-center Coulomb integrals are estimated by making use of the Slater-Condon parameters[20] F_2^{pp} and G_1^{sp} obtained from atomic spectra of neutral atoms:*2

$$\begin{aligned}(pp|p'p') &= F_0^{pp} - 2F_2^{pp}\\ (sp|sp) &= G_1^{sp}\\ (pp'|pp') &= 3F_2^{pp}\end{aligned} \quad (4)$$

where p and p′ are orthogonal to each other and F_0^{pp} is estimated by using the Pariser approximation. The integral (ss|pp) is taken as the arithmetic mean of (ss|ss) and (pp|pp).

5. Two-center Coulomb integrals are evaluated by using the following approximate formulas of Roothaan's exact ones[21] for several sub-integrals.*3

$$\begin{aligned}[3S|3S] &= \frac{1}{\rho}\left[1 - S^2/\{(1-\tau^2)^7\cdot(1+0.465\rho)\}\right]\\ [3S|1S] &= \frac{1}{\rho}\left[1 - \frac{S^2}{-0.2 + (1-1.66\tau)\rho}\right]\\ [3S|3D\Sigma] &= \frac{1}{(1-\tau)^2\rho^3}[1-S^2\cdot(1+0.5\rho)]\\ [3S|3P\Sigma] &= \frac{1}{(1-\tau)\rho^2}[1-S\cdot(1+0.12\rho)]\end{aligned} \quad (5)$$

Here S means the overlap integral between two s type AO's, $\tau=(\zeta_a-\zeta_b)/(\zeta_a+\zeta_b)$, ζ_a and ζ_b being taken as the orbital exponents of two AO's, and $\rho=R_{AB}(\zeta_a+\zeta_b)/2$, R_{AB} being the distance between atoms A and B. The following more approximate formulas are employed for other smaller sub-integrals.

$$\begin{aligned}[3P\Sigma|3P\Sigma] &= \frac{2}{\rho^3}(1-2S^2)\\ [3P\pi|3P\pi] &= \frac{1}{\rho^3}\left(1 - \frac{16}{\rho^3}\right)\\ [3D\Sigma|3D\Sigma] &= \frac{6}{\rho^5}\left(1 - \frac{3.76}{\rho^4}\right)\\ [3D\Delta|3D\Delta] &= \frac{1}{\rho^5}\left(1 - \frac{7.5}{\rho^2}\right)\end{aligned} \quad (6)$$

In method II, the semi-empirical values for these integrals are evaluated from the corresponding non-empirical values in method I by using the following formulas:

$$\begin{aligned}(s_As_A|p_Bp_B)^{emp} &= (s_As_A|p_Bp_B)^n\\ &\quad - \Big[\frac{1}{2}(s_A|s_B)^2\{(s_Bs_B|p_Bp_B)^n - (s_Bs_B|p_Bp_B)^{emp}\}\\ &\quad + (p_A|p_B)^2\{(s_As_A|p_Ap_A)^n - (s_As_A|p_Ap_A)^{emp}\}\\ &\quad + (s_A|p_B)^2\{(p_Bp_B|p_Bp_B)^n - (p_Bp_B|p_Bp_B)^{emp}\}\\ &\quad + (s_A|p_B)^2\{(s_As_A|s_As_A)^n - (s_As_A|s_As_A)^{emp}\}\Big]\\ (s_Ap_A|p_Bp_B)^{emp} &= (s_Ap_A|p_Bp_B)^n\\ &\quad - \Big[\frac{1}{2}(s_A|s_B)(p_A|s_B)\{(s_Bs_B|p_Bp_B)^n\\ &\quad - (s_Bs_B|p_Bp_B)^{emp}\}\\ &\quad + (s_A|p_B)(p_A|p_B)\{(p_Bp_B|p_Bp_B)^n\\ &\quad - (p_Bp_B|p_Bp_B)^{emp}\}\Big]\end{aligned} \quad (7)$$

Here superfixes emp and n mean empirical and non-empirical values, respectively. These formulas are obtained by expanding the AO of atom A with regard to the position of atom B.*4

6. The off-diagonal core integral (β_{ab}) between AO's a and b is evaluated by the following formula;

$$\beta_{ab} = C\cdot S_{ab}\left\{\left(a\left|\frac{Z_A}{R_{A\mu}}\right|a\right) + \left(b\left|\frac{Z_B}{R_{B\mu}}\right|b\right) - \left(a\left|\frac{Z_B}{R_{B\mu}}\right|a\right) - \left(b\left|\frac{Z_A}{R_{A\mu}}\right|b\right)\right\}\Big/4 \quad (8)$$

where C is an empirical parameter and is commonly taken $C=0.92$ for all molecules. S_{ab} is the overlap integral between AO's a and b. β_{ab} is taken for both neighboring and non-neighboring AO's.

Our treatment is similar to the NDDO (Neglect of Diatomic Differential Overlap) method of Pople *et al.*,[8] in the sense that the overlap integrals and the two-center differential overlaps are disregarded. The integrals of these two types may be expected to be cancelled out when Löwdin's orthogonalized

*1 The (pp|pp) type integrals are not so sensitive to the valence state of each atom.

*2 The use of F_2^{pp} and G_1^{sp} for neutral atoms seems to be incompatible with the fact that F_0 evaluated by the Pariser approximation is that of the corresponding anion. But F_2 and G_1 are so small that the difference between the neutral and anionic values may be safely disregarded.

19) R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953).

20) Concerning the use of this parameter, see for example, T. Anno, *ibid.*, **29**, 1161 (1958).

*3 The meaning of symbols like [3S|3S], [3S|3S], — are the same as described in Ref. 21.

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

*4 The formulas of this type were first used by Matsushita for the theoretical study of π-electron systems. T. Matsushita, private communication.

Table 1. One-center and two-center integrals calculated by the aid of the Slater AO's and the Löwdin OAO's

Type	AO integrals	OAO integrals
$(h\|H^{core}\|h)^0$*	−13.60	−12.45
$(p\|H^{core}\|p)^0$	−54.28	−51.40
$(hh\|hh)^0$	17.01	19.22
$(\sigma\sigma\|\sigma\sigma)^0$	16.93	18.42
$(\pi\pi\|\pi\pi)^0$	16.93	17.62
(hh|ss)	10.32	9.85
$(\sigma\sigma\|\sigma\sigma)$	11.92	11.30
$(\sigma\sigma\|\pi\pi)$	10.35	10.01
$(\pi\pi\|\pi\pi)$	9.35	9.13

* The estimation is made for the case of C_2H_4, the ls orbital exponent of hydrogen being taken to be 1.0, and 2s and 2p orbital exponents for carbon to be 1.59. Superscript 0 means the one-center integrals.

orbitals (OAO's)[22] are taken as the basis AO's as was pointed out by Fischer-Hjalmars[23] for π-electron systems. This cancellation may be expected to be less perfect for σ-orbitals than for π-orbitals, but this approximation is essential for the simplification of the calculation. Furthermore, we neglect the changes of the remaining integrals (except for β) caused by the transformation of the basis set from the Slater AO's to the OAO's.*5 According to our estimation, they are larger for σ-orbitals than for π-orbitals, but are not fatal as is shown in Table 1.

Since the Slater type 2s orbital is not orthogonal to the inner 1s orbital, the direct calculation leads to a too large absolute value of the one-center core integral for this orbital. The ionization potential for an electron in orbital x can be obtained by Koopmans' theorem[24] as the sum of the core integrals and electron repulsion part. Therefore, if the repulsive part is considered to be equal to each other for 2s and 2p electrons, the difference in the core integrals for these orbitals may be thought to be equal to that in the ionization potentials. Thus we obtain Eq. (2).

The approximations adopted to the evaluation of the two-center Coulomb integrals are not always necessary. In view of computational convenience, however, the present formulas are satisfactory from the practical point of view. The present approximate formulas are applicable to the rather small region of orbital exponents and atomic distances. In the sub-integrals of Roothaan's formulas which are common to several atomic integrals, the term including $\exp(-2\rho)$ is approximated by the term including the square of overlap integrals for the first four formulas. For other small sub-integrals, the more approximate formulas are employed. These formulas give the resultant integrals different by less than 6% from the exact values as is shown in Table 2.

Table 2. Comparison between approximate and exact integral values

Type[a]	Approximate values	Exact values
For Ethylene		
(ss|ss)	9.99 eV	9.98 eV
$(ss\|\pi\pi)$	9.56	9.47
$(\sigma\sigma\|\sigma\sigma)$	11.71	11.86
$(\pi\pi\|\pi\pi)$	9.14	9.42
$(\sigma\sigma\|\pi\pi)$	10.42	10.41
$(ss\|s\sigma)$	1.89	1.86
For CO of Formaldehyde		
(ss|ss)	11.23	11.22
$(ss\|\sigma\sigma)$	11.93	11.84
$(\sigma\sigma\|ss)$	12.61	12.56
$(\sigma\sigma\|\sigma\sigma)$	13.56	13.57
$(\pi\pi\|\pi\pi)$	10.28	10.40
$(\pi\pi\|\pi'\pi')$	10.03	10.10

a) Here, s, σ, π and π' mean 2s, $2p\sigma$, $2p\pi$ and $2p_y$ (y-axis is in the molecular plane) AO's, whose orbital exponents are determined following Slater's rule.

In the evaluation of the semi-empirical two-center Coulomb integrals in method II, the following three factors are considered. First the correlation effect discussed by many researchers,[25] second the effect of the reorganization of orbitals caused by the one-electron ionization or excitation,[26] and third the expansion of the excited orbitals.[27] These effects may affect two-center Coulomb integrals, even when overlap integrals are zero. By considering these effects we evaluated the integrals by Eq. (7) obtained by expanding the AO of atom A with regard to the position of atom B. When the same method is applied to π-electron systems, the evaluated values are somewhat larger than those obtained by the uniformly charged sphere model or by the Ohno approximation.[28]

The formula for the off-diagonal core integral is obtained by adopting the Mulliken approximation and by considering the effect of the orthogonalization to the first order of overlap integrals between

22) P. O. Löwdin, *ibid.*, **18**, 365 (1950).
23) I. Fischer-Hjalmars, *ibid.*, **42**, 1962 (1965).
*5 Cook, Hollis and McWeeny used the hybrid orbitals as basis AO's to avoid this difficulty, but their method is more complicated than ours (D. B. Cook, P. C. Hollis and R. McWeeny, *Mol. Phys.*, **13**, 553 (1967)).
24) T. Koopmans, *Physica*, **1**, 104 (1933).
25) See, for example, O. Sinanoglu, "Advances in Chemical Physics," Vol. VI, ed. by I. Prigogine, Interscience Publishers, London (1964), p. 315.
26) M. K. Orloff and O. Sinanoglu, *J. Chem. Phys.*, **43**, 49 (1965).
27) S. Huzinaga, *ibid.*, **36**, 453 (1962).
28) K. Ohno, *Theor. Chim. Acta* (Berl.), **2**, 219 (1964).

the nearest neighbouring atoms. The value of parameter C is optimized for the orbital energies of ethylene.

The computation is carried out by a HITAC 5020E electronic computer located at the Computer Center of the University of Tokyo. Several quantities are calculated with the aid of the evaluated orbital wavefunctions and energies. The atomic

TABLE 3. ORBITAL ENERGIES (eV) OF C_2H_4

Symmetry[a]	Method I	Method II	CNDO[b]	Y-Y-K[c]	Non-empirical[d]	Inoization[e] potential (eV)
$b_{1u}(\pi)$	−10.96	−11.85	−10.93	−12.24	−10.17	10.48
b_{1g}	−12.59	−13.39	−10.98	−13.98	−14.00	12.51
a_g	−15.00	−14.06	−13.01	−13.75	−15.81	14.9
b_{2u}	−18.90	−18.41	−17.15	−15.65	−17.81	15.63
b_{3u}	−22.62	−20.42	−19.48	−19.70	−21.66	19.13
a_g	−30.60	−25.07	−26.01	−24.09	−28.29	—

a) The molecular plane is taken to be xy plane and x axis is parallel to the C=C bond.
b) Ref. 13.
c) Ref. 16.
d) J. M. Schulman, J. W. Moskowitz and C. Hollister, *J. Chem. Phys.*, **46**, 2759 (1967).
e) Ref. 30.

TABLE 4. ORBITAL ENERGIES (eV) OF H_2CO

Symmetry[a]	Method I	Method II	Y-Y-K[b]	Non-empirical[c]	Ionization[d] potential (eV)
$b_1(n)$	−11.99	−11.71	−13.36	−10.76	10.86
$b_2(\pi)$	−14.07	−13.91	−14.28	−13.53	14.4
a_1	−15.44	−16.10	−14.85	−16.14	16.0
b_1	−18.85	−20.03	−21.84	−18.40	16.9
a_1	−23.31	−24.21	−22.15	−22.62	21
a_1	−36.80	−37.82	−34.06	−38.07	—

a) The molecular plane is taken to be xy plane and x axis is parallel to the C=O bond.
b) Ref. 16.
c) M. D. Newton and W. E. Palke, *J. Chem. Phys.*, **45**, 2329 (1966).
d) Ref. 31.

TABLE 5. ORBITAL ENERGIES OF CO

Character	Method I	Method II	Y-Y-K[a]	Non-empirical[b]	Ionization[c] potential (eV)
σ	−14.50	−14.09	−14.43	−15.08	14.01
π	−16.33	−15.42	−15.32	−17.40	16.51
σ	−21.11	−22.14	−20.50	−21.87	19.72
σ	−42.73	−40.03	−35.17	−41.39	—

a) Ref. 16.
b) A. D. McLean and M. Yoshimine, "Table of Linear Molecule Wavefunctions," *IBM J. Research and Development* (1967).
c) Ref. 30.

TABLE 6. ORBITAL ENERGIES OF HCN

Character	Method I	Method II	CNDO[a]	Non-empirical[b]	Ionization[c] potential (eV)
π	−14.52	−13.42	−13.33	−13.48	13.91
σ	−15.80	−15.31	−13.72	−15.83	
σ	−22.93	−21.63	−20.69	−22.69	
σ	−35.73	−34.81	−27.60	−33.60	

a) Ref. 12.
b) Ref. b in Table 5.
c) J. D. Morrison and A. J. C.Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

population of a certain AO is calculated as the sum of the square of the coefficients of the corresponding AO in the occupied MO's. This definition coincides with Mulliken's gross or net atomic population in this case in which overlap integrals are disregarded. Dipole moments are calculated by the method proposed by Pople and Segal.[9] Excitation energies are calculated by considering the configuration interaction among several singly excited configurations of lower energy.

Results and Discussion

In this section, we present the results obtained by applying the above-mentioned two methods to several small molecules and compare them with those of other calculations and also with the experimental results.

Orbital Energies. In Tables 3—6 are shown the occupied orbital energies calculated by the present authors. In these tables the results calculated by other theoretical methods are also shown for the purpose of comparison, together with the observed ionization potentials which correspond to the absolute values of orbital energies according to Koopmans' theorem.[24] Recently, the ionization potentials higher than the first one are measured by the photo-electron spectroscopy technique for various molecules.[29,30]

Concerning ethylene (Table 3), the original CNDO/2 parameters failed in giving the orbital energies in correct order. Modifying the parameters, Sichel and Whitehead[13] obtained by the CNDO method the results which are fairly in good agreement with the observed ionization potentials, but the separation between the highest and second highest occupied orbitals is still too small. In the result of the Y-Y-K method, the order of the second highest and third highest occupied orbitals is reverse to that obtained by the other methods. Either of the present results obtained by methods I and II is generally in rather good agreement with the result obtained by the non-empirical calculation and with the observed ionization potentials. In particular, it may be noticed that the present methods lead to better agreement with the ionization potentials for the higher three orbital energies than the other non-empirical or semi-empirical methods.

The result of ethylene obtained by method II shows rather smaller orbital energy separations compared with that of method I. This tendency holds for formaldehyde, carbon monoxide and hydrogen cyanide, too. Anyhow, from the results in Tables 3—6, it is revealed that both the empirical and non-empirical Coulomb integrals in the present methods are applicable to the theoretical prediction of ionization potentials.

Charge Density. The charge density on the hydrogen atom in several molecules are listed in Table 7. The present results as well as those by the other methods show that the positive charge on hydrogen increases in the order of $CH_4 < C_2H_4 < C_2H_2$. This is coincident with the fact that the hydrogen atom of acetylene is rather easily replaced by metal and also with the fact that the dipole moments of C–H bonds in these molecules estimated from the absolute intensities of the infrared absorption spectra[31] increase in the same order. Comparing the results of methods I and II with each other, the former gives a little smaller values for all molecules under consideration than the latter. The results of INDO[32] calculation give considerably large values compared with those by other methods.

In Table 8, the calculated atomic population of ethylene is shown. Our results show rather good agreement with those of the non-empirical calculation except for the population on the 2p orbital. The value calculated by the present method is smaller than that by the non-empirical one, but

Table 7. Charge density on H

	Method I	Method II	CNDO[a]	Non-empirical	INDO[d]
CH_4	0.941	0.988	0.987	0.87[b]	1.009
C_2H_4	0.891	0.920	0.985	0.86	1.001
C_2H_2	0.887	0.901	0.937	0.81	0.947
HCN	0.876	0.904	0.928	0.78	—
H_2CO	0.917	0.931	1.001	0.90[c]	—

a) Ref. 10.
b) W. Palke and W. Lipscomb., *J. Amer. Chem. Soc.*, **88**, 2384 (1966).
c) P. L. Goodfriend, F.W. Birss and A.B.F. Duncan, *Rev. Mod. Phys.*, **32**, 307 (1960).
d) W. J. Hehre and J. A. Pople, *Chem. Phys, Lett.*, **2**, 379 (1968).

Table 8. Atomic population of ethylene

	Method I	Method II	PNDDO[a]	Non-empirical[b]
H	0.899	0.920	0.985	0.860
C_{2s}	1.194	1.149	1.243	1.197
$C_{2\sigma}$	1.017	1.008	0.844	1.013
C_{2y}	0.990	1.002	0.845	1.072

a) Ref. 15 (PNDDO means Partial Neglect of Diatomic Differential Overalp).
b) Ref. b in Table 7.

29) M. I. AL-Joboury and D. W. Turner, *J. Chem. Soc.*, **1964**, 4434.
30) G. R. Brundle and D. W. Turner, *Chem. Commun.*, **7**, 314 (1967).
31) L. A. Gribov and V. N. Smirnov, *Soviet Physics Uspekhi*, **4**, 919 (1962).
32) J. A. Pople, D. L. Beveridge and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

TABLE 9. ATOMIC POPULATION OF H_2CO

	Method I	Method II	CNDO[a]	Non-empirical[b]
H	0.917	0.931	0.958	0.90
s_c	1.230	1.230	1.184	1.42
σ_c	0.819	0.837	0.958	0.63
y_c[c]	0.980	0.985	0.990	1.01
s_o	1.862	1.853	1.731	1.97
σ_o	1.300	1.336	1.348	1.08
y_o[c]	1.963	1.932	1.926	1.98
π_c	0.990	0.981	0.978	1.04
π_o	1.010	1.019	1.022	0.96

a) Ref. 9.
b) Ref. c in Table 7.
c) The direction of y is prependicular to the C=O bond in the molecular plane.

TABLE 10. ATOMIC POPULATION OF CO

AO	Method I	Method II	CNDO[a]	Non-empirical[b]
s_c	1.59	1.63	1.70	1.68
σ_c	0.96	0.97	1.08	0.96
s_o	1.84	1.80	1.70	1.85
σ_o	1.69	1.52	1.51	1.51
π_c	0.65	0.69	0.65	0.63
π_o	1.31	1.35	1.35	1.37

a) Ref. 9.
b) R. Ransil, *J. Chem. Phys.*, **30**, 1113 (1959).

not so extremely small as the result by Dewar and Klopman.[15]

In Table 9, the atomic population of formaldehyde is shown. According to our results the population on the $p\pi$ orbital is larger for oxygen than for carbon. This is reverse to the results by the non-empirical calculation. In the other points, the atomic populations of formaldehyde calculated by the present method are well coincident with those by the non-empirical calculation.

TABLE 11. DIPOLE MOMENTS OF SOME SIMPLE MOLECULES

Molecule	Method I	Method II	CNDO[a]	Exp.[b]
CO	−1.40	−1.56	−1.28	−0.13
NH_3	3.01	1.80	1.99	1.47
H_2CO	3.22	2.97	1.27	2.30
HCN	4.10	3.10	2.07	2.95

a) Ref. 9.
b) A.L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman & Co., San Francisco, California (1963).

Now let us turn to the atomic population of carbon monoxide shown in Table 10. According to our calculation, the oxygen atom is negatively charged in accordence with the non-empirical calculation, while the CNDO method leads to the reverse result. Concerning the total electron density on the oxygen atom, the result of method I (6.15) is well coincident with that of the non-empirical calculation (6.10) and method II gives a little smaller value (6.02). Since the same tendency is also found for the result by the Y-Y-K method, this seems to be an intrinsic to the use of the empirical integral values.

As a general tendency found for the calculated atomic populations, method II gives the smaller value for the population of 2s orbital than the non-empirical calculation. This is probably because the diagonal core integrals for 2s are a little underestimated (in absolute values) in method II.

The calculated dipole moments of several mo-

TABLE 12. EXCITATION ENERGIES (eV)

	Symmetry of excited state	Character of transition	Method I	Method II	Number of configuration**	Exp.
C_2H_4	$^3B_{3u}$	π-π^*	6.70	4.45	(4)	4.6[a]
	$^1B_{3u}$	π-π^*	10.80	7.84	(4)	7.6[b]
H_2CO	$^3A_2$	n-π^*	4.98	4.17	(4)	3.0[c]
	$^1A_2$	n-π^*	8.46	5.32	(4)	4.2[d]
	$^1A_1$	π-π^*	11.38	9.86	(3)	8.0[d]
CO	$^3\Pi$	n-π^*	8.73	7.10	(4)	6.22[e]
	$^1\Pi$	n-π^*	11.57	8.90	(4)	8.74[e]
	$^3\Sigma^+$	π-π^*	11.55	7.60	(3)	8.25[e]
	$^1\Sigma^+$	π-π^*	13.92	9.41	(3)	10.8[e]

** The number of configurations taken in the configuration interaction calculation is shown in parentheses.
a) D. F. Evans, *J. Chem. Soc.*, **1960**, 1735.
b) P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, **23**, 1895 (1955).
c) A. D. Cohen and C. Reid, *ibid.*, **24**, 85 (1956).
d) H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941).
e) H. Brion and C. Moser, *J. Chem. Phys.*, **32**, 1194 (1960).

lecules are shown in Table 11 compared with the experimental values. We can find a parallelism between the calculated and experimental values, though the former values are generally larger than the latter. Generally speaking, the dipole moment values calculated by method I are better coincident with experimental ones than those by method I.

Excitation Energies. In Table 12, the excitation energies calculated for ethylene, formaldehyde and carbon monoxide are listed. In the both methods the calculated energies are too high compared with the experimental results. This point may be improved by selecting the optimum β_{ab} value for the calculation of excited state quantities.

According to method I, the lowest singlet and triplet excited states of ethylene include σ—σ^* excited configurations by 30 and 22%, respectively, and the separation between them is a little improved by the configuration interaction compared with the single configuration picture. The separation is evaluated to be 4.16 and 3.39 eV by methods I and II, respectively. The latter is well coincident with the observed value (3.0 eV). The situation is the same for the separation between the singlet and triplet $n\rightarrow\pi^*$ states of formaldehyde. That is to say, the value calculated by method II agrees well with the observed one, though the value evaluated by method I is somewhat larger than the experimental value.

Concerning the orbital energies and atomic populations, the both methods give similarly good results, while method II is better for the excitation energies than method I. It may be noticed that method I gives fairly satisfactory results for the quantities of the ground state, in spite of its simplicity and the great reduction in the calculation time compared with the non-empirical calculation.