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# Semi-Empirical SCF Molecular Orbital Treatment for Valence Electron Systems. I. Small Molecules*[1]

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A semi-empirical SCF method for valence electron systems is presented. In the present method, the one-center integrals are estimated by means of the empirical values, while the two-center Coulomb integrals are calculated by the Ohno approximation. The other electronic repulsion integrals are evaluated by the Mulliken approximation. All overlap integrals in the secular equation are taken into account. By the present method, the electronic structures of several small polyatomic molecules are then studied. The calculated results are compared with the full SCF calculations and with the experimental values. The agreements between them are almost entirely satisfactory. The limitations of this method and the values of the parameters used are also discussed briefly.

Semi-empirical SCF molecular orbital methods have been successfully applied to various $\pi$-electron systems. The results of these calculations enable us to make more quantitative disccusions of the electronic absorption spectra, the charge distributions, and so on. Recently, attempts have been made to extend similar method to the treatment of the systems including $\sigma$ electrons or composed of all valence electrons by several authors.[1-8] That is, Klopman,[1] Pohl *et al.*,[2] and Rein and Harris[3] have proposed simplified SCF methods for simple $\sigma$-bonded systems. Allinger and Tai,[4] Imamura *et al.*,[2] and Katagiri and Sandorfy[6] calculated the $\sigma$ electronic structures of some simple compounds by adopting the hybridized orbitals as the bases. Recently, Pople and his coworkers have presented an approximate method for all valence electron systems, but this method neglects the overlap integrals.[7,8] Their treatment gives fairly reasonable molecular orbitals and electron distributions, but it fails to predict bond lengths and dissociation energies.

The present paper will present a semi-empirical SCF MO treatment in which all valence electrons in a compound are taken into account and all overlap integrals are included. The molecules treated are some simple polyatomic molecules. The calculated results, orbital energies, and charge distributions will be then compared with those obtained by more rigorous method or experiments.

## Theoretical

The molecular orbitals (MO's), $\varphi$'s, are taken as linear combinations of all the valence atomic orbitals (AO's), $\chi_r$'s, centered on the various atoms of the molecule:

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*1 A part of this paper was presented at the symposium on the electronic structure of molecules, Nagoya, October, 1965.

1) G. Klopman, *J. Am. Chem. Soc.*, **86**, 4550 (1964).

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

3) R. Rein and F. E. Harris, *ibid.*, **41**, 3393 (1964).

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

5) A. Imamura, M. Kodama, Y. Tagashira and C. Nagata, *J. Theoret. Biol.*, **10**, 356 (1966).

6) S. Katagiri and C. Sandorfy, *Theoret. Chim. Acta (Berl.)*, **4**, 203 (1966).

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

8) J. A. Pople and G. A. Segal, *ibid.*, **43**, s136 (1965).

$$\varphi_i = \sum_r C_{ir}\chi_r \tag{1}$$

The total Hamiltonian, $H$, is given by (in atomic units):

$$H = \sum_\mu H^{\mathrm{core}} + \sum_{\mu<\nu} \frac{1}{r_{\mu\nu}}$$

$$H_\mu{}^{\mathrm{core}} = -\frac{1}{2}\Delta(\mu) - \sum_{\mathrm{A}} \frac{Z_{\mathrm{A}}}{r_{\mu\mathrm{A}}} \tag{2}$$

where $Z_{\mathrm{A}}$ is the number of the valence electrons in atom A, and $r_{\mu\mathrm{A}}$ is the distance between the $\mu$th electron and atom A.

For a closed-shell molecule, the Roothaan SCF equation⁹⁾ is written as follows:

$$\sum_r C_{ir}(F_{rs} - S_{rs}\varepsilon) = 0 \quad (s = 1, 2, \cdots) \tag{3}$$

where:

$$F_{rs} = H_{rs} + \sum_{t,u} P_{tu}(rs|tu) - 1/2(rt|su)]$$

$$S_{rs} = \int \chi_r \chi_s \mathrm{d}\tau$$

$$H_{rs} = \int \chi_r(\mu) H\mu^{\mathrm{core}} \chi_s(\mu) \mathrm{d}\tau_\mu$$

$$(rs|tu) = \int \chi_r(\mu)\chi_s(\mu) \frac{1}{r_{\mu\nu}} \chi_t(\nu)\chi_u(\nu) \mathrm{d}\tau_\mu d\tau_\nu$$

$$P_{tu} = 2\sum_i^{\mathrm{occ}} C_{it}C_{iu}$$

The atomic integrals which appear in the above equations are evaluated by the following approximations: For the electron repulsion integrals, $(rs|tu)$, the Mulliken approximation¹⁰⁾ is adopted; therefore,

$$(rs|tu) = (1/4)S_{rs}S_{tu}[(rr|tt) + (rr|uu) + (ss|tt) + (ss|uu)] \tag{4}$$

The two-center Coulomb repulsion integrals, $(rr|ss)$, for the homopolar case are calculated by the Ohno approximation:¹¹,³⁾

$$(rr|ss) = 1/\sqrt{a^2 + (R_{rs})^2} \tag{5}$$

$$1/a = (rr|rr) = I_r - A_r$$

where $(rr|rr)$ denotes the one-center Coulomb integrals, and where $I_r$ and $A_r$ are the valence state ionization potential and the electron affinity respectively of the $r$th AO. For the heteropolar case, they are arithmetic means of the appropriate homopolar values.

An alternative equation¹²⁾ (M–N approximation) to evaluate $(rr|ss)$ written as:

$$(rr|ss) = \frac{1}{R+a} \tag{5'}$$

may be applicable. In the present treatment, however, Eq. (5) is adopted instead of Eq. (5′) for the reason stated in the next section.

On these assumptions at the first stage, the one-center exchange integrals are neglected for the sake of simplicity.[*2]

The $H_{rr}$ term in Eq. (3) is given by:

$$\begin{aligned} H_{rr} &= \int \chi_r(\mu)\Big(-\frac{1}{2}\Delta(\mu) - \frac{Z_{\mathrm{A}}}{r_{\mu\mathrm{A}}}\Big)\chi_r(\mu)\mathrm{d}\tau_\mu \\ &\quad - \sum_{\mathrm{B}\neq\mathrm{A}} \chi_r(\mu)\frac{Z_{\mathrm{B}}}{r_{\mu\mathrm{B}}}\chi_r(\mu)\mathrm{d}\tau_\mu \\ &= U_{rr} + \sum_{\mathrm{B}\neq\mathrm{A}} (B|rr) \end{aligned} \tag{6}$$

where:

$$U_{rr} = \int \chi_r(\mu)\Big(-\frac{1}{2}\Delta(\mu) - \frac{Z_{\mathrm{A}}}{r_{\mu\mathrm{A}}}\Big)\chi_r(\mu)\mathrm{d}\tau_\mu$$

$$(\mathrm{B}|rr) = -\int \chi_r(\mu)\frac{Z_{\mathrm{B}}}{r_{\mu\mathrm{B}}}\chi_r(\mu)\mathrm{d}\tau_\mu$$

With above approximations for one-center repulsion integrals, $U_{rr}$ is approximated by the next simple form:

$$U_{rr} = -I_r - (N_r - 1)(rr|rr) - \sum_{r'\neq r} N_{r'}(rr|r'r')$$

$$(rr|r'r') = (1/2)[(rr|rr) + (r'r'|r'r')] \tag{7}$$

where $N_r$ and $N_{r'}$ denote the number of electrons occupying the AO $r$ and $r'$ respectively of the same atom at the valence state, and where $\sum_{r'\neq r}$ denotes the summation over all the valence AO's of the atom in question except for AO $r$.[*3]

The core attraction integrals of the $(\mathrm{B}|rr)$ type are approximately replaced by their corresponding repulsion integrals:

$$(\mathrm{B}|rr) = -Z_{\mathrm{B}}(s_{\mathrm{B}}s_{\mathrm{B}}|rr) \tag{8}$$

where $s_{\mathrm{B}}$ refers to the valence $s$ orbital on atom B.

For the off-diagonal elements, $H_{rs}$ $(r \neq s)$, we adopt a formula which is analogous to the approximation by Wolfsberg and Helmholtz:¹³⁾

$$H_{rs} = 0.5\,KS_{rs}(H_{rr} + H_{ss}) \tag{9}$$

where $K$ is a constant taken to be 1.1 in the present calculations. The details of this will also be given in the next section.

The values of $I_r$, $A_r$ and the effective nuclear charge, $Z_{\mathrm{A}}{}^*$, are summarized in Table 1, where $I_r$ and $A_r$ for the 2p orbitals of the oxygen atom are

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9) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

10) R. S. Mulliken, *J. Chem. Phys.*, **46**, 497, 675 (1949).

11) K. Ohno, *Theoret. Chim. Acta (Berl.)*, **2**, 219 (1964).

12) N. Mataga and K. Nishimoto, *Z. physik. Chem. N. F.*, **13**, 140 (1957).

[*2] The calculations, including those of the one-center exchange integral, will be presented in the near future.

[*3] The one-center Coulomb integrals of the $(rr|r'r')$ type, where $r$ and $r'$ refer to the different AO's on the atom, become equal to each other when $r$ and $r'$ denote the px, py or pz orbitals.

13) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

TABLE 1. VALENCE STATE IONIZATION POTENTIAL ($I_r$), ELECTRON AFFINITY ($A_r$) AND EFFECTIVE NUCLEAR CHARGE ($Z_A$*) OF AO's

| | | $Z_A$* | $I_r$†(eV) | $A_r$†(eV) |
|---|---|---|---|---|
| H | s †† | 1.00 | 13.60 | 0.747 |
| C | p | 3.25 | 11.42 | 0.58 |
| | s | | 21.43 | 9.26 |
| N | p | 3.90 | 14.49 | 1.58 |
| | s | | 27.50 | 13.79 |
| O | p | 4.55 | 15.45 | 1.73 |
| | s | | 35.30 | 19.85 |

† These values, except for 2p AO's of the oxygen atom, are quoted from Pritchard and Skinner's table. (*Chem. Revs.*, **55**, 745 (1955.))

†† The notations s and p denote the valence s p AO's of the atoms.

TABLE 2. THE CALCULATED RESULTS BY VARIOUS PARAMETER VALUES FOR ETHYLENE MOLECULE

| Ohno approximation | | | | |
|---|---|---|---|---|
| $K$* | 1.08 | 1.1 | 1.15 | 1.2 |
| $N$ | 9 | 8 | 6 | 6 |
| $I_p$ | 11.70 | 12.24 | 13.54 | 14.77 |
| $T$ | 4.45 | 5.68 | 8.76 | 10.83 |
| $V$ | 7.91 | 9.14 | 12.24 | 14.19 |
| $Q_C$ | −0.171 | −0.177 | −0.172 | −0.163 |

| | M–N approximation | | | Obs.[1] |
|---|---|---|---|---|
| $K$* | 1.1 | 1.15 | 1.2 | — |
| $N$ | 14 | 11 | 10 | — |
| $I_p$ | 10.78 | 11.80 | 12.82 | 10.52 |
| $T$ | 4.31 | 6.89 | 9.46 | 4.8 |
| $V$ | 7.10 | 9.68 | 12.25 | 7.6 |
| $Q_C$ | −0.110 | −0.125 | −0.140 | — |

* $K$=The values of $K$.
$N$=The number of iterations.
$I_p$=ionization potential (eV).
$T$=triplet $\pi$-$\pi$* transition energy (eV).
$V$=singlet $\pi$-$\pi$* transition energy (eV).
$Q_C$=net charge of carbon atom.

1) J. W. Moskowitz and M. C. Harrison, *J. Chem. Phys.*, **42**, 1726 (1965).

average values as estimated by a method similar to that described in Ref. 14. For the geometries of the treated compounds, the latest data from Ref. 15 are adopted.

The starting set of coefficients of MO, $C_{it}$'s, are obtained by Hoffmann's method.[16] About 8—15 iterations suffice to obtain a convergence to within 0.0001 of all the MO energies.

## Estimation of Basic Integrals

For the semi-empirical SCF calculation for valence electron systems, numerous procedures are possible when one combines various approximations in evaluating basic atomic integrals appearing in the calculation. Several attempts have been made of determine the best approximation; these attempts have been successful to some extent. However, further investigations are needed before we can draw any final conclusion. In this conection, it seems worthwhile to state our reasons for adopting Eq. (5) and $K$=1.1 in the present treatment.

Based upon the approximation stated above, some calculations were made, with the various $K$ values in Eq. (9) and with two different formulas, to estimate the two-center repulsion integrals, Eqs. (5) and (5′).

The calculated results for the ethylene molecule are collected in Table 2, together with the observed values. That is, the iteration number ($N$); the ionization potential ($I_p$), the singlet $\pi$-$\pi$* transition energy ($V$), the triplet transition energy ($T$), and the net charges on the carbon atom ($Q_C$) are given in the table, together with the adopted approximations and $K$ values. For $K$=1.0 and $K$=1.2, the results seem unreasonable and the convergence are very poor. The results using the M–N approximation with $K$=1.1 and the Ohno approximation with $K$=1.08 agree fairly well with the observed values, while those obtained using the approximation with $K$=1.1 are the second best in Table 2. For the methane molecule, the convergence obtained using the M–N approximation ($K$=1.1) is very poor ($N$=20), whereas the iteration number obtained using the Ohno approximation ($K$=1.1) is only 10 and the obtained results are almost satisfactory. For the compounds with the hetero atoms, the convergences are more difficult.

Accordingly, in those calculations for small molecules, the Ohno approximation and the value of $K$=1.1 are adopted. In Table 2 it may be noticed that the values of the transition energy are largely dependent on the values of $K$, while, on the other hand, the charge distributions are almost independent of the $K$ values.

## Results and Discussion

In this section, the calculated results for some small molecules will be compared with those obtained by more accurate methods and experiments.

**Orbital Energy.** The occupied MO energies (in eV) calculated by the present method are compared with the results of non-empirical calculations in Table 3. The agreement between them seems

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14) E. B. Moore, Jr., *J. Chem. Pys.*, **43**, 503 (1965).

15) "Table of Interatomic Distances and Configuration in Molecules and Ions," ed. by A. D. Mitchell, The chemical Society, London (1958).

16) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

TABLE 3. OCCUPIED MO ENERGIES (eV) FOR VARIOUS MOLECULES

(a) $CH_4$

| | Present calc. | Ref. a | Obs.* |
|---|---|---|---|
| $t_2$ | −13.70 | −13.24 | −13.16 |
| $a_1$ | −21.50 | −25.04 | −19.42 |

a) J. J. Sinai, *J. Chem. Phys.*, **39**, 1575 (1963).
* D. C. Frost and C. A. McDowell, *Proc. Roy. Soc.*, **A241**, 194 (1957).

(b) $C_2H_6$

| Staggered | | | Eclipsed | | |
|---|---|---|---|---|---|
| | Present calc. | Ref. b | | Present calc. | Ref. b |
| $a_{1g}$ | −13.32 | −14.59 | $a_1'$ | −13.31 | −14.56 |
| $e_g$ | −13.93 | −14.01 | $e''$ | −13.84 | −13.94 |
| $e_u$ | −15.60 | −17.07 | $e'$ | −15.64 | −17.08 |
| $a_{2u}$ | −20.89 | −23.37 | $a_2''$ | −20.87 | −23.34 |
| $a_{1g}$ | −24.21 | −28.30 | $a_1'$ | −24.19 | −28.27 |

b) R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963).

(c) $C_2H_4$

| | Present calc. | Ref. c |
|---|---|---|
| $b_{1u}$ | −12.24 | −9.97 |
| $a_g$ | −13.75 | −15.49 |
| $b_{1g}$ | −13.98 | −13.88 |
| $b_{2u}$ | −15.65 | −17.62 |
| $b_{3u}$ | −19.70 | −21.61 |
| $a_g$ | −24.09 | −28.31 |

c) J. W. Moskowitz, *J. Chem. Phys.*, **43**, 60 (1965).

(d) CO

| | Present calc. | Ref. d | Obs.* |
|---|---|---|---|
| $5\sigma$ | −14.43 | −13.74 | −14.01 |
| $1\pi$ | −15.32 | −16.60 | −16.92 |
| $4\sigma$ | −20.50 | −20.65 | −19.90 |
| $3\sigma$ | −35.17 | −41.76 | — |

d) H. Brion and C. Moser, *J. Chem. Phys.*, **32**, 1194 (1960).
* See Ref. d.

(e) $H_2CO$

| | Present calc. | Ref. e | Obs.* |
|---|---|---|---|
| $b_1$** | −13.36 | −11.53 | −10.83 |
| $b_2$*** | −14.28 | −15.08 | −11.8 |
| $a_1$ | −14.85 | −19.25 | −13.1 |
| $b_1$ | −11.84 | −21.94 | — |
| $a_1$ | −22.15 | −22.10 | — |
| $a_1$ | −34.06 | −38.73 | — |

e) P. L. Goodfriend, F. W. Birss and A. B. F. Duncan, *Rev. Mod. Phys.*, **32**, 307 (1960).
* See J. M. Parks and R. G. Parr, *J. Chem. Phys.*, **32**, 1657 (1960).
** Lone-pair orbital.
*** $\pi$-MO.

(f) $H_2O$

| | Present calc. | Ref. f | Obs.* |
|---|---|---|---|
| $b_2$ | −12.88 | −11.84 | −12.6 |
| $a_1$ | −13.48 | −13.20 | −14.5 |
| $b_1$ | −14.66 | −18.64 | −16.2 |
| $a_1$ | −32.50 | −38.23 | — |

f) F. O. Ellison and H. Shull, *J. Chem. Phys.*, **23**, 2348 (1955).
* See Ref. f.

(g) $NH_3$

| | Present calc. | Ref. g | Obs.* |
|---|---|---|---|
| $a_1$ | −12.21 | −14.00 | −11.0 |
| e | −13.79 | −19.31 | −17.0 |
| $a_1$ | −24.95 | −32.60 | — |

g) H. K. Kaplan, *J. Chem. Phys.*, **26**, 1704 (1957).
* H. Sun and G. L. Weissler, *ibid.*, **23**, 1160 (1955).

TABLE 4. CALCULATED AND OBSERVED IONIZATION POTENTIALS (eV)

| Compound | Calc. | Obs. |
|---|---|---|
| $CH_4$ | 13.70 | 13.16[a*] |
| $C_2H_6$ | 13.32 | 11.78[*1] |
| $C_2H_2$ | 12.44 | 11.42[*1] |
| $C_2H_4$ | 12.24 | 10.52[*2] |
| CO | 14.43 | 14.01[d] |
| $CO_2$ | 15.11 | 13.79[*3] |
| $H_2O$ | 12.88 | 12.6[f] |
| $H_2CO$ | 13.36 | 10.83[e] |
| $CH_3OH$ | 12.54 | 10.88[*1] |
| HCN | 13.94 | 13.86[*4] |
| $NH_3$ | 12.21 | 11.0[g] |

* The alphabets denote the each reference in Table 3.
[*1] A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).
[*2] See Ref. 1 in Table 2.
[*3] W. C. Price and D. M. Simpson, *Proc. Roy. Soc.*, **A169**, 501 (1939).
[*4] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

fairly good. Especially, the energy levels of lone-pair orbitals for $H_2CO$, $NH_3$ and so on seem reasonable, whereas in Hoffmann's method they lie in too-low energy regions, as has already been pointed out in one of our previous papers.[17] As to the energy difference between the staggered and eclipsed ethane, the calculated energy of the staggered form is less than that of the eclipsed form by 6.6 kcal/mol, where the experimental value is 3.0 kcal/mol.[18] However it may be noted that the symmetries of the highest occupied orbitals in

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[17] K. Morokuma, H. Kato, T. Yonezawa and K. Fukui, This Bulletin, **38**, 1263 (1965).
[18] D. R. Lide, *J. Chem. Phys.*, **29**, 1426 (1958).

TABLE 5. CALCULATED VALUES OF VARIOUS TRANSITION ENERGIES (eV) OF SOME MOLECULES

| Compound | Type of transition | Calc. | Obs. |
|---|---|---|---|
| $C_2H_4$ | $(\pi-\pi^*)^{3,*}$ | 5.68 | 4.8$^{a)}$ |
| | $(\pi-\pi^*)^3$ | 9.15 | 7.6 |
| | $(\sigma_{b1g}-\pi^*)^{3,1}$ | (7.82)** | — |
| | $(\sigma_{ag}-\pi^*)^{3,1}$ | (8.25) | — |
| $H_2CO$ | $(n\pi-^*)^3$ | 4.26 | 3.0$^{b)}$ |
| | $(n-\pi^*)^1$ | (4.26) | 4.2 |
| | $(\pi-\pi^*)^3$ | 5.24 | 4.2 |
| | $(\pi-\pi^*)^1$ | 9.01 | 8.0 |
| CO | $(n-\pi^*)^3$ | 5.06 | 6.22$^{c)}$ |
| | $(n-\pi^*)^1$ | (5.06) | 8.74 |
| | $(\pi-\pi^*)^3$ | 6.17 | 8.25 |
| | $(\pi-\pi^*)^1$ | 8.76 | 10.8 |
| $H_2O$ | $(n-\sigma^*)^{1,3}$ | (9.66) | 7.4$^{d)}$ |

a) J. W. Moskowitz and M. C. Harrison, *J. Chem. Phys.*, **42**, 1726 (1964).

b) J. M. Parks and R. G. Parr, *ibid.*, **32**, 1657 (1960).

c) See Ref. d in Table 3.

d) A. D. Walsh, *J. Chem. Soc.*, **1953**, 2260.

* The numbers 1, 3 refer to singlet and triplet transitions respectively.

** The parenthesis refers to that the exchange integral, $K_{ij}$ is calculated to be zero in this transition.

the present treatment do not agree with those obtained in non-empirical calculations. Further discrepancies as to the energies of the lowest occupied orbitals are observed in our results in Table 3, which are generally higher than those obtained in more rigorous calculations.

For the ionization potentials, the calculated and observed values are listed in Table 4. In general, the calculated values of the hydrocarbons are about 1—2 eV larger than the observed values, but a good parallelism is found between them.

The energies in various types of excitations can be obtained by the present method. The calculated results for some molecules and the observed values are collected in Table 5. The excitation energies in the present method run parallel with the observed values, but the calculated values are about 1—2 eV larger than the observed values in ethylene, formaldehyde, and water molecules. Further, the singlet and triplet transitions in some types (for example, the $n$-$\pi^*$ transition) can not be distinguished by the present approximations.[*4]

**Charge Distribution.** In Table 6, the calculated values of the AO population in several compounds are presented together with the other results. The agreement between the two sets of results is fairly satisfactory. For instance, the difference in the corresponding AO populations

TABLE 6. AO POPULATIONS FOR $C_2H_6$, CO AND $H_2CO$

(a) $C_2H_6$

| | | $h$ | $s_C$ | $\sigma_C$ | $\pi_C$ |
|---|---|---|---|---|---|
| Eclipsed | Present calc. | 0.925 | 1.237 | 0.942 | 1.024 |
| | Ref. b* | 0.886 | 1.278 | 0.969 | 1.045 |
| Staggered | Present calc. | 0.927 | 1.237 | 0.943 | 1.020 |
| | Ref. b* | 0.887 | 1.280 | 0.971 | 1.043 |
| | Ref. 8 | 0.967 | 1.042 | 1.044 | 1.007 |

* Ref. b in Table 3.

(b) CO

| | $S_C$ | $\sigma_C$ | $\pi_C$ | $S_O$ | $\sigma_O$ | $\pi_O$ |
|---|---|---|---|---|---|---|
| Present calc. | 1.567 | 0.939 | 0.649 | 1.905 | 1.589 | 1.350 |
| Ref. d* | 1.664 | 0.930 | 0.619 | 1.862 | 1.543 | 1.381 |
| Ref. 8 | 1.697 | 1.088 | 0.620 | 1.702 | 1.512 | 1.380 |
| Ransil** | 1.68 | 0.96 | 0.63 | 1.85 | 1.51 | 1.37 |

* Ref. d in Table 3.

** B. J. Ransil, *J. Chem. Phys.*, **30**, 1113 (1959).

(c) $H_2CO$

| | $s_C$ | $\sigma_C$ | $\pi_C$ | $\pi'_C$ | $h$ | $s_O$ | $\sigma_O$ | $\pi_O$ | $\pi'_O$** |
|---|---|---|---|---|---|---|---|---|---|
| Present calc. | 1.232 | 0.637 | 0.992 | 0.982 | 0.907 | 1.870 | 1.512 | 1.008 | 1.953 |
| Ref. e* | 1.42 | 0.63 | 1.04 | 1.01 | 0.90 | 1.97 | 1.08 | 0.96 | 1.98 |
| Ref. 8 | 1.132 | 0.958 | 0.978 | 0.990 | 0.958 | 1.731 | 1.348 | 1.022 | 1.926 |

* Ref. e in Table 3.

** lone-pair orbital.

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[*4] They correspond to the transitions between the states belonging to different symmetries with respect to the molecular plane. This is due to the approximations adopted in Eqs. (4) and (7).

TABLE 7. AO BOND POPULATIONS IN ETHANE

| | | | Eclipsed | | | | |
|---|---|---|---|---|---|---|---|
| Present calc. | $s_{C1}$ | $\sigma_{C1}$ | $\pi_{C1}$ | Ref. b* | $s_{C1}$ | $\sigma_{C1}$ | $\pi_{C1}$ |
| $s_{C2}$ | 0.0610 | 0.1500 | 0 | $s_{C2}$ | 0.0179 | 0.2032 | 0 |
| $\sigma_{C2}$ | 0.1500 | 0.3940 | 0 | $\sigma_{C2}$ | 0.2032 | 0.3647 | 0 |
| $\pi_{C2}$ | 0 | 0 | −0.0300 | $\pi_{C2}$ | 0 | 0 | −0.0126 |
| $h$ | 0.2322 | 0.0532 | 0.5314 | $h$ | 0.2062 | 0.0589 | 0.5249 |

| | | | Staggered | | | | |
|---|---|---|---|---|---|---|---|
| Present calc. | $s_{C1}$ | $\sigma_{C1}$ | $\pi_{C1}$ | Ref. b* | $s_{C1}$ | $\sigma_{C1}$ | $\pi_{C1}$ |
| $s_{C2}$ | 0.0614 | 0.1492 | 0 | $s_{C3}$ | 0.0180 | 0.2031 | 0 |
| $\sigma_{C2}$ | 0.1492 | 0.3946 | 0 | $\sigma_{C2}$ | 0.2031 | 0.3650 | 0 |
| $\pi_{C2}$ | 0 | 0 | −0.0220 | $\pi_{C2}$ | 0 | 0 | −0.0089 |
| $h$ | 0.2322 | 0.0532 | 0.5286 | $h$ | 0.2058 | 0.0589 | 0.5220 |

* See Ref. b in Table 3.

between the staggered and eclipsed ethane molecules are of the same orders in both the present and non-empirical SCF calculations. Pople and Segal predicted that some amount of $\pi$ bond order in the C–C bond exists in the ethane molecule.[8] As is shown in Table 7, however, our results, like those of Pitzer and Lipscomb show that the $\pi$ bond population in this bond is small and negative; that is, the C–C bond in this molecule does not exhibit the $\pi$ bond character. Similarly, the $\pi$ bond population in three equivalent C–C bonds of cyclopropane is found to be as −0.018. For the formaldehyde molecule, the $\pi'$ bond order of the C–O bond (in the molecular plane) is calculated to be 0.27 in Ref. 8; the corresponding value in this treatment is 0.021.

In Table 6 it may be seen that our calculated values of the atom population on the oxygen or nitrogen atoms seem to be somewhat larger than the other results. Actually, the dipole moments which are obtained by utilizing Eq. (4.1) and Eq. (4.2) in Ref. 8,[*5] are about 1 Debye (D) larger than the experimental values, as may be seen in Table 8. For the hydrogen atoms in some hydrocarbons, our AO populations and the charge densities calculated in Ref. 8 are collected in Table 9. Both sets of results show that the charges on hydrogen atoms decrease with an increase in the s-characters of carbon atoms. For the cyclopropane, its hydrogen charges are remarkably positive; this result may be correlated with the extraordinary electro-negative character of the ring carbons.

TABLE 8. CALCULATED AND OBSERVED DIPOLE MOMENTS (Debye)

| Compound | $\mu_Q$* | Calc. $\mu_{atom}$*(sp) | $\mu_{total}$* | Obs.** $\mu$ |
|---|---|---|---|---|
| $H_2CO$ | 0.82 | 2.23 | 3.05 | 2.30 |
| CO | 1.06 | −2.09 | −1.03 | −0.13 |
| $H_2O$ | 0.97 | 1.95 | 2.92 | 1.84 |
| $NH_3$ | 1.46 | 1.65 | 3.11 | 1.47 |
| HCN | 2.67 | 1.67 | 4.34 | 2.95 |

* These notations refer to the difinitions in Ref. 8.
** Values appeared in Ref. 8.

TABLE 9. CHARGES OF HYDROGEN ATOMS

| Compound | Present calc. | Ref. 8 |
|---|---|---|
| $CH_4$ | 0.952 | 0.965 |
| stag.-$C_2H_6$ | 0.927 | 0.967 |
| $C_2H_4$ | 0.918 | 0.954 |
| $C_3H_6$ | 0.914 | — |
| $C_2H_2$ | 0.842 | 0.893 |

It should be stressed that though our computation times are only a few dozen of those possible in non-empirical calculations, the presented semi-empirical SCF treatment gives almost satisfactory results. Some refinements for the evaluation of the integrals or the parameters used are now in progress. These results will be published in the near future.

The calculations have been carried out on an IBM 7090 computer at the Japan IBM Co., with the permission of the UNICON committee, and on an HITAC 5020 computer at the computation center of the University of Tokyo.

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[*5] For the evaluation of the dipole moments, we use the atom population instead of the charge density, $P_{AA}$, in Eq. (4.1) of Ref. 8.